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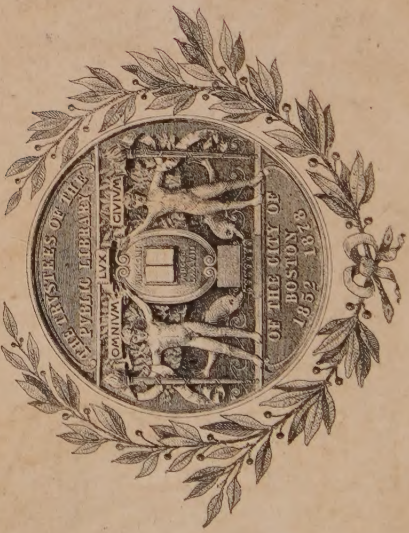

No 7789.5

Practical Pharmaceutical Chemistry.

AN EXPLANATION

OF

CHEMICAL AND PHARMACEUTICAL PROCESSES,

WITH THE

METHODS OF TESTING THE PURITY OF THE PREPARATIONS.

DEDUCED FROM ORIGINAL EXPERIMENTS.

BY DR. G. C. WITTSTEIN.

TRANSLATED AND EDITED FROM THE SECOND GERMAN EDITION,

BY STEPHEN DARBY,

PRACTICAL PHARMACEUTIST.

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INTRODUCTION

BY DR. A. BUCHNER, SEN.

THE work of a professor whose reputation is so widely extended as that of the author of this Pharmaceutical Text Book, has little need of an introduction from a writer of longer standing. Inasmuch, however, as the scientific labours of Wittstein have hitherto been imparted to the public through my "Repertorium für der Pharmacie;" and, as this, the first complete work emanating from his pen, contains embodied in it the results of lengthy and important chemical investigations, which for several years he has undertaken and carried out at my suggestion, and mostly under my own supervision; it will not appear presumptuous for me to bear testimony to its peculiar value, and, at his earnest request, write a Preface to it.

The book contains a mass of new facts, and includes none but the results of his own chemical inquiries, an advantage which gives it a peculiar character, and imparts to it an especial value at the present time, when, as regards chemistry and pharmacy, works of mere compilation are so abundant. Another recommendation is the scientific spirit which animates the investigations, and which cannot fail to incite the youthful reader to follow in the same path of inquiry. It will be at once perceived that the author is a skilful and accurate manipulator, who possesses the power of imparting his own information and ideas in a

clear comprehensive style, enabling any one but little practised to perform each chemical operation with ease and certainty. The qualitative relations of the whole of the different agents and products are based upon stochiometrical calculations, a matter of the highest practical value. It would be impossible too strongly to recommend this work to the beginner, for the clearness and completeness of its explanations, and as an example of accuracy of detail,—by following which he will become well grounded in practical chemistry;—the theoretical explanation of the chemical processes,—the stochiometrical formulas elucidating all the preparations,—and the datas for testing the purity of them, being eminently calculated to assist him in obtaining such an advantage.

The practical chemist will certainly derive assistance from the accuracy of the author, and from the peculiarity of his hints, which may be unknown to, or forgotten by, many,—whilst the relative product, being in each case faithfully appended, serves to control the cost of corresponding experiments, and enable its cost to be calculated. Every chemist who makes use of this book will regret that Wittstein, instead of extending his practical experience, his observations, his improvements, and calculations to other chemicals, has confined them to pharmaceutical preparations, especially as the practical opportunities which he enjoyed are by no means frequent.

I hope that this useful book, which contains the valuable and abundant results of the daily labours of some years, may meet with the encouragement it merits, and serve as a text-book to numberless manipulators, both teachers and learners.

Munich.

PREFACE TO THE FIRST EDITION.

I HAVE for several years, at different times, published in the "Repertorium für der Pharmacie" some of the results of my daily occupation, under the title of "Practical Explanations of Chemical and Pharmaceutical Principles." My motive has been no idle desire for literary fame, but a wish to impart to others what appeared to me the value or worthlessness of those processes to which, in repeatedly making preparations, I have given a trial. With pleasure I perceived that these little notices were not unfavourably received. I gradually increased their number, and reserved to myself the idea of one day publishing them together in a complete form. The time has now arrived in which I feel enabled to do this.

The contents of the following pages are clearly and entirely explained in their title. I have not pretended to write an introduction to Pharmacy (of such books there is no dearth), but my intention has been to impart such information as is seldom to be found in these works; as, for instance, a critical explanation of the different methods of making preparations; which method is to be preferred, and the advantages which characterize it; a practical account of the points to be observed in the manipulation (on which frequently a successful result depends); the theory of the several processes; and finally, the tests for detecting impurities and adulterations. It is by instituting experiments that deficiencies are discovered; and

the number of new facts this book contains is by no means small. All other matter, such as the history, literature, and application of the preparations, I have in most cases omitted, as extending beyond the limits of the present work.

Amongst the preparations, I have included some which possess a purely chemical or technical interest; but I hope that the practical pharmaceutist will find I have omitted none respecting which, as being required in medicine, they may desire advice. I can, moreover, add the assurance that every method has been tried by myself, and most of them repeatedly; whilst my long practice will give me the right of passing an opinion on them.

The arrangement of the book I made a secondary consideration; as being the most convenient form, I have chosen an alphabetical one, and also classed each preparation according to its Latin name, to which is appended its ordinary synonyme, and German appellation. As a further assistance, a complete Latin and German index is appended to the end.

THE AUTHOR.

Munich.

PREFACE TO THE SECOND EDITION.

THE summons which a year ago I received from the Publishers to prepare a Second Edition of this Treatise on preparation, gave me the agreeable assurance that the First Edition, in spite of its many imperfections, had found admission to many pharmaceutical laboratories. I determined, as well as correcting it as much as possible, to make several additions of those new compounds of which I had carefully tested the properties and methods of preparation; at the same time it gave me the opportunity of paying due regard to the hints of friendly reviewers. In the general arrangement of the work, however, I considered it better to make no alteration.

I trust that the Second Edition may enjoy the same indulgent criticism and reception as the first.

THE AUTHOR.

Munich, October, 1850.

TRANSLATOR'S PREFACE.

THE real merits of the present work have been so clearly shown in the Prefaces by the Author and Professor Buchner, as to require no further notice from me. My motive in translating it has been the hope of supplying,—what I felt was so much wanted in this country,—a book of *Practical Pharmaceutical Chemistry.* From the minuteness of the practical and theoretical explanations of each article, the work, as far as it extends, is complete in itself, and forms a sure basis to a more extended knowledge of scientific Chemistry. Having spent some large portion of my time in the Laboratory, I know full well the advantage of deriving explanations from practical men and original papers.

Simply to reduce the price, and place the present work within the reach of all, I have omitted such matter as, bearing more on scientific Chemistry, is not absolutely necessary for a pharmaceutist, but which I think some day to publish as a supplement to the present volume.

In conclusion, I must crave the indulgence of my readers, and trust that the merits of the work will induce them to overlook any imperfections in the translation, which has been carried out in my hours of relaxation from business.

S. D.

140, *Leadenhall Street,* 1853.

EQUIVALENT NUMBERS

OF THE

SIMPLE BODIES

ON WHICH THE DIFFERENT CALCULATIONS ARE BASED.

	Oxygen 100.	Hydrogen 1.
Aluminium	171	13·67
Antimony	806	64·48
Arsenic	470	37·60
Barium	856	68·48
Bismuth	1330	106·40
Boron	136	10·88
Bromine	1000	80·00
Cadmium	700	56·00
Calcium	250	20·00
Carbon	75	6·00
Cerium	590	47·20
Chlorine	443	35·44
Chromium	334	26·72
Cobalt	369	29·52
Copper	396	31·68
Didymium	620	49·60
Fluorine	236	18·88
Glucinium	87	6·96
Gold	1230	98·40
Hydrogen	12·5	1·00
Iodine	1586	126·88
Iridium	1232	98·56
Iron	350	28·00
Lanthanum	588	47·04
Lead	1294	103·52
Lithium	82	6·56
Magnesium	158	12·64
Manganese	345	27·60
Mercury	1250	100·00
Molybdenum	576	46·08
Nickel	370	29·52
Osmium	1243	99·44
Oxygen	100	8·00
Nitrogen	175	14·00
Palladium	666	53·28
Phosphorus	200	16·00
Platinum	1232	98·56
Potassium	490	39·20
Rhodium	652	52·16
Ruthenium	651	52·08
Selenium	495	39·60
Silver	1350	108·00
Silicium	277	22·16
Sodium	290	23·20
Strontium	546	43·68
Sulphur	200	16·00
Tantalum	1148	91·84
Tellurium	802	64·16
Thorium	744	59·52
Tin	725	58·08
Titanium	302	24·16
Uranium	743	59·44
Vanadium	856	68·48
Wolfram	1188	95·04
Yttrium	403	32·24
Zinc	407	32·56
Zircon	420	33·60

ERRATA.

Page	11	*line*	29	*for*	Sn_2Cl_2	*read*	$SnCl_2$.
—	19	—	6	—	bibulrus . . .	—	bibulous.
—	47	—	20	—	$HO + \bar{L} + HO$	—	$HO = \bar{L} + HO$.
—	95	—	3	—	nitrate . . .	—	nitrite.
—	121	—	32	—	sulphuric . .	—	valerianic.
—	156	—	16	—	*protoxide of* .	—	*no protoxide of.*
—	192	—	19	—	secretion . . .	—	reaction.
—	198	—	4	—	nitrate of strontian	—	chloride of strontium.
—	201	—	17	—	chlorate of baryta	—	chlorate of ammonia.
—	252	—	20	—	sulphurous . .	—	sulphuric.
—	367	—	6	—	sulphur . . .	—	potash.
—	379	—	21	—	effloresced . .	—	deflagrated.
—	476	—	26	—	caustic potash	—	potashes.
—	500	—	18	—	$\overline{Mo}$	—	$\overset{+}{Mo}$.
—	523	—	31	—	sulphate . . .	—	sulphite.
—	600	—	3	—	latter	—	former.

*** The reader is particularly requested to make the above corrections.

CHEMICAL AND PHARMACEUTICAL PROCESSES.

ACETON.

Hydrated Oxyde of Mesityle.

FORMULA: C_3H_3O; or, $C_6H_5O + HO$.

Preparation.—A convenient quantity of acetate of lead is put into a black lead retort, of such a capacity that it is only half filled; the retort is placed in a blast furnace, and supported on bricks; to its neck an earthen or glass tube is luted, and connected by means of bladder in which a few small needle punctures have been made, with a capacious receiver. Hot charcoal is now placed around the retort, which is at first to be very slowly warmed, and the fire gradually increased until it reaches a red heat, when a portion of liquid will pass over. During the process the receiver must be kept very cool. When no more drops of water are deposited in the neck of the receiver, the apparatus is allowed to cool. The contents of the retort, which from 20 parts of acetate of lead will amount to about 4 or $4\frac{1}{2}$ parts, is shaken with hydrate of lime, to neutralize the free acid, and then distilled in a glass retort until about two-thirds have passed over. The distilled portion is the Liquor pyro-aceticus.

In order to obtain pure acetone this must be digested with half its weight of fused chloride of

calcium, then distilled in a water bath until half the liquid has passed over, again shaken in a closed vessel with half its weight of fused chloride of calcium, and allowed to deposit; the upper portion is then decanted from the, more or less moist, chloride of calcium and rectified; the retort being this time placed in a water bath, and the process stopped as soon as its contents cease to boil. The distilled portion is to be kept in a well-stopped bottle. 20 Parts of sugar of lead will yield about 1 part of acetone.

Any other acetate, as acetate of lime for instance, may be substituted for sugar of lead; but the latter is to be preferred on account of its cheapness. By the addition of caustic lime to the sugar of lead, as recommended by Zeise, I have obtained no greater yield than with the latter substance alone.

Recapitulation of the Process.—When sugar of lead ($PbO + \bar{A} + 3HO$) is subjected to a gradually increasing heat, it fuses to a colourless liquid, which froths up and loses its water, as well as a trace of acetic acid; the dry white mass which now remains in the retort will dissolve again in water almost entirely, the solution having an acid reaction, consequently it consists of anhydrous neutral acetate of lead. By raising the heat this white mass liquefies, acid vapours are given off, smelling slightly of acetic acid, but more pungent (acetone); the mass changes to a somewhat gray colour, again solidifies to a grayish white residue, which is partly soluble in water and of an alkaline reaction. The sugar of lead, after the loss of the water, is converted into a basic salt, and free acetic acid; but, owing to the high temperature, the greater part of the latter is instantaneously decomposed, forming other products. Now, on raising the fire almost to a red heat, the acetic acid, still combined with lead, is given off in its decomposed state, without the mass being again fused; the residue acquires a grayish

yellow colour, and consists of a mixture of carbonate of lead, oxide of lead, and metallic lead, which last partly collects in a fluid form at the bottom. By allowing access of air the yellowish gray mass gradually assumes a reddish yellow colour, being entirely converted into oxide of lead.

If we compare this behaviour of sugar of lead when heated, with the appearances which present themselves in the preparation of acetone, we shall find that at first scarcely anything but water is given off; and on account of the frothing which results from it, the heat must at the beginning be very gently applied; then follow the products of the decomposition of the acetic acid, accompanied by a small portion of this acid, which passes over as such, having escaped decomposition. The volatile products are principally acetone, carbonic acid, water, and an empyreumatic oil. The acetone is thus formed; the acetic acid loses one atom of carbon and two of oxygen, thus :—

$C_4H_3O_3$ divides into
C_3H_3O and CO_2;

part of the carbonic acid combines with the oxide of lead, the remainder escapes. Another portion of acetic acid is decomposed into an empyreumatic oil :—C_6H_5O, water and carbonic acid, thus :—

2 at. $C_4H_3O_3$, form
1 at. C_6H_5O, 1 at. HO, and 2 at. CO_2.

Finally, the carbon of a third portion of acetic acid decomposes the carbonic acid, water and carbonic oxide being formed, which latter reduces a certain portion of oxide of lead, as shown in the following formula :—

1 at. $C_4H_3O_3$, and 4 at. PbO, form
3 at. HO, 4 at. CO, and 4 at. Pb.

That a considerable portion of acetic acid is evolved,

as such, and transformed into other products than acetone and carbonic acid, the following consideration will demonstrate. 2370 Parts (1 atom) of crystallized sugar of lead contain 658 parts of anhydrous acetic acid in which exist the elements of 363 parts of acetone and 275 parts of carbonic acid. 2370 Parts of sugar of lead should, therefore, other considerations apart, produce 363 parts, or nearly $\frac{1}{6}$ of anhydrous acetone; yet, in fact, we obtain only $\frac{1}{8}$ of this presumed yield; or from $\frac{1}{15}$ to $\frac{1}{20}$ of the weight of sugar of lead; $\frac{2}{3}$ of the acetic acid in the sugar of lead is lost, of which the greater portion is not simply volatilized, but transformed, into the above-mentioned products of decomposition. Thus but a small portion of lime is necessary to neutralize the acid in the first distillate. The acetate of lime which is formed remains in the retort with a portion of water and empyreumatic oil, when about $\frac{2}{3}$ of the neutralized liquid has distilled over. The distilled portion is the medicinal Liquor pyro-aceticus. In order to deprive it entirely of water and empyreumatic oil, it is rectified in a water bath over chloride of calcium; when about half has passed over, all the oil and water will remain behind; and at this point the distillation must be stopped, as the receiver will now contain all the acetone. By treating the second time with chloride of calcium, and rectifying in a water bath, the last trace of water is removed.

Properties.—Pure acetone is a colourless, mobile liquid, having a peculiar ethereal odour, reminding one of acetic ether, and faintly empyreumatic, with a pungent taste. Its spec. grav. is 0·80. It boils at 132° Fah.; it is mixible, in all proportions, with water, alcohol, and ether; ignites readily, and burns with a bright flame.

The Liquor pyro-aceticus has a yellowish tinge, possesses the properties of acetone, but, of course, in a lower degree, and is more empyreumatic to the taste. Its spec. grav. is 0·90.

ACIDUM ACETICUM CONCENTRATUM.

Acetum Concentratum.—Concentrated Acetic Acid.

FORMULA : $C_4H_3O_3 + xHO = \bar{A} + xHO$.*

Preparation.—In a tubulated retort, large enough to hold twice the quantity of substances employed, 15 parts of powdered acetate of lead are placed, and to this is added 4 parts of concentrated sulphuric acid (English), previously mixed with three parts of water and cooled. A leaden vessel is the best to mix the acid and water in, there being no fear of its cracking on account of the rise of temperature, or of contaminating the liquid, as when cast-iron vessels are used. The retort is now carefully agitated until a uniform mixture is obtained; it is then placed in a sand bath, and connected with a capacious glass receiver, into nearly the centre of which the retort neck should reach. That part of the retort neck in contact with the receiver is surrounded with a strip of white paper, which fixes them more firmly, and renders them less liable to crack than when the two glass surfaces are in contact. The retort, which should rest on a bed of sand $\frac{1}{2}$ an inch thick, and with which it is now surrounded to a level with the contents, is heated gently, and the fire gradually increased. As soon as the receiver becomes warm, a continuous stream of cold water is allowed to flow on it till the process is ended. The fire is continued until the residue appears dry, and no more drops are visible at the beak of the retort. When the apparatus is

* xHO signifies here, as in all other formulas in which it is expressed, a quantity of water commensurate with the state of concentration of the preparation. Prepared according to the formula here given, the concentrated acetic acid would contain about 10 HO.

thoroughly cooled, the contents of the receiver are poured into a glass-stoppered bottle. The produce should be 9 parts of acetic acid.

Distillation over a naked fire, although preferable in many other cases, is not admissible in the preparation of acetic acid from sugar of lead, as in order to obtain all the acetic acid a slight excess of sulphuric acid is employed, which, when all the acetic acid had distilled, might, at that temperature, possibly pass over and contaminate the product. With a sand heat this is not to be feared, if the above-mentioned quantity of sulphuric acid is not exceeded.

If the quantity of sugar of lead employed does not exceed 1 pound, the residue is easily removed from the retort by shaking with water. When operating with large quantities it is more difficult, and in this case the use of a little sulphate of soda is a great assistance. By adding to the acetate of lead before distilling $\frac{1}{12}$ its weight of effloresced Glauber's salt, the insoluble residue in the retort is more readily removed by water, which, dissolving the Glauber's salt, loosens the whole.

Acetic acid is also advantageously prepared from the impure dried acetate of soda. On 5 parts of this salt, a mixture of 6 parts of concentrated sulphuric acid and 5 parts of water is poured, and the distillation proceeded with as in the preceding case. The produce should be $8\frac{1}{2}$ parts.

Recapitulation.—Sugar of lead consists of 1 at. oxide of lead (PbO), 1 at. acetic acid ($C_4H_3O_3 = \bar{A}$), and 3 at. water (HO) = PbO + $\bar{A}$ + 3HO, the equivalent number of which is 2370; the concentrated sulphuric acid consists of 1 at. sulphuric acid (SO_3), and 1 at. water (HO) = SO_3 + HO, its equivalent is is 613. When brought into contact, the sulphuric acid, on account of its greater affinity for the oxide of lead, combines with it to form a white insoluble

salt, which remains behind on heating, whilst the acetic acid passes off.

One atom of sugar of lead requires exactly one atom of hydrated sulphuric acid entirely to decompose it.

1 at. $PbO + \bar{A} + 3HO$, and 1 at. $SO_3 + HO$, form

1 at. $PbO + SO_3$, 1 at. $\bar{A}$, and 4 at. HO.

2370 Parts of the first require, therefore, 613 parts of acid, or 15 parts, require 3·87 parts. In the above process rather more is ordered; instead of 3·87, 4 parts are taken, because the commercial English sulphuric acid generally contains somewhat more than 1 at. of water; and whilst, with proper caution, a slight excess of sulphuric acid is not prejudicial, it is desirable that no acetate of lead remain undecomposed.

All the water contained in the sugar of lead and sulphuric acid, as that employed to dilute the latter, distils over with the acetic acid. This, from 15 parts of sugar of lead, is 2·1, from 4 of sulphuric acid 0·7 parts, which, with the 3 parts added, make 5·8 parts. In 15 parts sugar of lead are contained 4 parts of acetic acid; the distilled product must consequently yield 9·8 parts, supposing all loss to be avoided.

The sulphate of lead in the retort, after washing and drying, can be used as a painter's colour, or be converted into chromate of lead by digestion with chromate of potash.

In order to decompose 1 at. of acetate of soda entirely over a sand bath, it is necessary to use 2 at. of sulphuric acid, and thus to convert it into the bi-sulphate.

1 at. $NaO + \bar{A}$, and 2 at. $SO_3 + HO$, form

1 at. $NaO + 2SO_3 + HO$, 1 at. $\bar{A}$, and 1 at. HO.

1028 Parts of anhydrous acetate of soda require 1226 parts of concentrated sulphuric acid, or 5 parts

of the first and 6 of the acid. The 5 parts of water, mixed with the acid, correspond to 9 at.; and as the sulphuric acid also gives up 1 at. of water, (the other atom of water from the 2 atoms of sulphuric acid combining with the bi-sulphate of soda,) 10 at. of water distil over with the acetic acid. The common acetate of soda generally contains a small quantity of extractive matter, and, towards the end of the process, the action of the sulphuric acid on it causes a blackening of the contents of the retort, with, at the same time, a disengagement of sulphurous acid, which renders the product impure. In this case, the distillate is shaken with a little peroxide of manganese (MnO_2), by which the sulphurous acid is converted into sulphuric and hyposulphuric acids, and these combine with the oxide of manganese, formed:—

2 at. MnO_2 and 3 at. SO_2, form
1 at. $MnO + SO_3$ and 1 at. $MnO + S_2O_5$.

The liquid is poured off the excess of peroxide of manganese, and re-distilled. The bi-sulphate of soda remaining in the retort readily dissolves in water, and the solution filtered from the insoluble black organic matter, may, after neutralization with lime, be used as Glauber salts.

Properties.—Acetic acid is colourless, and of a pure, strong, acid smell and taste, free from empyreumatic odour. Prepared according to the preceding directions, it has a spec. grav. of 1·045, and 2 parts must entirely neutralize 1 part of dry carbonate of potash; it contains about 64 per cent. of acid, or 10 at. of water. No residue should occur on evaporation. Sulphuretted hydrogen, nitrate of baryta, nitrate of silver, and ferrocyanide of potassium should cause no change in it. If it contain *empyreumatic matter*, it may be detected by the smell and discoloration on the addition of concentrated sulphuric acid. *Sugar*, in a more or less changed

condition, is an impurity occasionally met with in commercial acetic acid, (evidently arising from the dilution of strong vinegar with that from starch sugar;) this is known by a brownish yellow syrup, of a sweet bitter taste, like burnt sugar, remaining on evaporation. Also, on neutralizing such acetic acid with alkalies and evaporating, dark brown or blackish salts are formed, arising from the action of the alkali on the sugar. If a milkiness is caused by sulphuretted hydrogen, the presence of *sulphurous acid* is denoted from the partial decomposition of the sulphuric acid, which always occurs when acetates not free from colouring matter have been used. The milkiness is occasioned by the hydrogen of the sulphuretted hydrogen combining with the oxygen of the sulphurous acid to form water, whilst the sulphur from both, combined with a little sulphuretted hydrogen, is precipitated as milk of sulphur:—

1 at. SO_2 and 2 at. SH, form
2 at. HO and 3 at. S.

If sulphuretted hydrogen causes a blackening, *lead* or *copper* may be present (the hydrogen of the sulphuretted hydrogen combines with the oxygen of the oxide of copper or lead forming water, whilst the sulphur goes to the metal); if it arises from lead, sulphuric acid causes a white precipitate of sulphate of lead; if from copper, supersaturation with ammonia imparts a blue colour, (combination of oxide of copper with ammonia.) A white precipitate on the addition of nitrate of baryta, insoluble in nitric acid, denotes *sulphuric acid*, whilst *hydrochloric acid* is present if nitrate of silver gives a white casiform precipitate insoluble in nitric acid and becoming violet when exposed to the light. (In this case the oxygen of the oxide of silver combines with the hydrogen of the hydrochloric acid, forming water, and the silver with the chlorine, leaving the

nitric acid free.) With ferrocyanide of potassium a reddish brown colour indicates *copper;* a blue one, *iron.* To explain these phenomena we must consider the iron and copper to exist as acetates. The potassium of the cyanide of potassium, existing in the ferrocyanide, extracts the oxygen of the oxide of copper or iron, and combines with the acid of these metallic salts, forming acetate of potash; the copper or iron thus deprived of its oxygen and acid combines with the cyanogen liberated, to form a cyanide of copper or iron, and being seized upon by the ferrocyanogen of ferrocyanide of potassium is precipitated as ferrocyanide of copper or ferrocyanide of iron (Prussian blue). In order to explain this complex decomposition, we will turn to the chemical formulas of the salts and their products.

1 at. $(2KCy + FeCy)$ and 2 at. $CuO + \bar{A}$), form
2 at. $(KO + \bar{A})$ and 1 at. $(FeCy + 2CuCy)$.

3 at. $(2KCy + FeCy)$ and 2 at. $(Fe_2O_3 + \bar{A}_3)$, form
6 at. $(KO + \bar{A})$ and 1 at. $(3FeCy + 2Fe_2Cy_3)$,

Purification.—From non-volatile impurities the acetic acid is very readily freed by simple rectification in glass vessels; if sulphuric or hydrochloric acid is present, a little sugar of lead is added previous to distillation; and for sulphurous acid, peroxide of manganese. The latter acts by converting the sulphurous acid into sulphuric and hyposulphuric at the expense of part of its oxygen, and being reduced to the protoxide, combines with the acids formed. The sugar of lead combines with the hydrochloric or sulphuric acid, giving off its own acetic acid. Empyreumatic matter is removed by shaking with rather coarse, freshly-heated, wood charcoal, filtering and rectifying the filtrate. This latter process is necessary to separate any inorganic constituents that the acids may have extracted from the charcoal.

The tests for the concentrated acetic acid also apply to the dilute, which must give no precipitate with the before-mentioned reagents. A good vinegar must be colourless or only slightly yellow, and so strong that 2 ounces entirely neutralize 1 drachm of carbonate of potash. By evaporation it almost always leaves a brown extractive residue, arising partly from the materials used in the fermentation, and partly from its preparation and preservation in wooden vessels. If sulphuretted hydrogen gives a brown precipitate, this may be from the presence of *tin*, and the vinegar has probably been distilled in a vessel with a tin head and refrigerator. The brown precipitate is proto-sulphuret of tin, and is formed from the protoxide of tin dissolved in the acid. The protoxide of tin will be more readily detected by the addition of a solution of chloride of gold, which causes the deep purple precipitate known as purple of Cassius, of the composition of this substance only this much is known, that it contains gold, tin and oxygen. If we consider these three elements grouped so as to form oxide of gold $=AuO$, and oxide of tin $=Sn_2O_3$, and further, that previously to the reaction the tin existed in the solution as an acetate of the proto and peroxide, we shall find that—

2 at. (Au_2Cl_3) and 14 at. $(Sn_2O_3 + 3\bar{A})$, form 4 at. $(AuO + 3Sn_2O_3)$ = purple of Cassius, 3 at. (Sn_2Cl_2), 1 at. $(SnO_2 + \bar{A}_2)$, and 40 at. $\bar{A}$, liberated.

Especial care must be taken to test vinegar for adulterations which are added with the view of imparting to it an artificial acidity or sharpness. Of acids added with a fraudulent intention, the hydrochloric and sulphuric are most common on account of their cheapness,—the higher price of nitric and tartaric renders their use less probable. Should only a slight turbidness be caused by nitrate of

baryta or nitrate of silver, it must not be considered as a fraudulent adulteration, because most vinegar is prepared with well or spring water, which always contains traces of chlorides or sulphates: these, of course, will be found in the vinegar. We can at once decide that it is adulterated, should the beforementioned reagents give a dense precipitate; still it is better to proceed as follows:—

4 ounces of vinegar are placed in a retort, with a receiver attached, and distilled to dryness, then heated so long as anything passes over. If *free sulphuric* acid be present, a portion of it, being deprived by the organic matter of part of its oxygen, will be found as sulphurous acid, and detected by its odour in the distillate, which also will contain sulphuric acid, as nitrate of baryta will indicate. Another still more convenient method is, to mix 1 ounce of vinegar with some grains of white sugar, and evaporate at a very gentle heat; should free sulphuric acid be present, the residue, so soon as it attains the thickness of an extract, will acquire a deep black colour. In this case the sugar becomes decomposed, its hydrogen and oxygen, as water, being abstracted by the sulphuric acid and the carbon liberated. To detect *free hydrochloric* acid, the vinegar, when about half distilled over, is tested with nitrate of silver; or, 4 ounces of vinegar are, with $\frac{1}{2}$ ounce of peroxide of manganese, poured into a flask and a glass tube attached, the other end of which dips into a glass filled with water, in which a few drops of solution of indigo are dissolved, and the contents of the flask brought to the boiling point. If free hydrochloric acid be present, the oxygen of the peroxide of manganese will deprive it of its hydrogen, one half of the liberated chlorine combines with the manganese, the other half passes over; and so soon as it comes in contact with the indigo solution, the latter will be destroyed and the water become decolorized; on

the further evolution of chlorine, the water will be coloured yellow and acquire the well-known smell of the gas. The operation is finished when about half the vinegar has passed over.

The vinegar may also be adulterated with pungent vegetable matter, as capsicums or spurge laurel roots. Such a vinegar neutralized with carbonate of potash loses its sour taste, whilst the pungency arising from the falsification becomes still more apparent. The detection is more certain if the vinegar is first reduced by evaporation to one-fourth, and then neutralized and tasted.

ACIDUM ACETICUM CRYSTALLIZATUM.

Acidum aceticum glaciale.—Crystallized acetic acid.—Hydrated acetic acid.

FORMULA: $\bar{A} + HO = C_4H_3O_3 + HO$.

Preparation.—6 parts of sugar of lead are rubbed to a fine powder in a porcelain mortar, the powder thinly spread on a flat porcelain dish or plate, and perfectly dried by gently heating on a sand-bath. The powder is now injected into a thoroughly-dried tubulated retort, the latter connected, by means of a moistened bladder in which a few fine holes are made, with an equally dry receiver, and the retort closed with a good cork, through which is inserted the lower end of a doubly bent funnel tube (see the accompanying figure). The retort is very gently warmed in the sand bath, and, by means of the funnel tube, 8 parts of fuming sulphuric acid are gradually added. Directly the acid comes in

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contact with the lead salt, thick white fumes are evolved and slowly pass into the receiver, which must be kept very cool. As soon as all the acid is added the process is assisted by a very gentle fire, which is continued so long as the fumes are given off; when this ceases the apparatus is allowed to cool. In order to render the product quite pure, the white crystalline mass in the receiver is quickly rubbed with about one fourth of its weight of finely-powdered and well-dried peroxide of manganese, the mixture placed in a retort connected with a receiver,—both must be thoroughly clean and dry,—and the retort gently heated in a sand bath so long as white vapours are given off. The receiver is disconnected, and warmed to liquefy its contents, which are poured into a thoroughly dry bottle, having a well-ground glass stopper.

The dried common acetate of soda may also be advantageously employed in this process: 5 parts of it require 6 of fuming sulphuric acid, and the process is carried on according to the previous directions.

Recapitulation.—This process is essentially the same as that given for the preparation of concentrated acetic acid. In order, however, to obtain the mono-hydrated acetic acid, the sugar of lead must be well dried to free it from its water of crystallization, the sulphuric acid used containing as much water as is required by the acetic acid, whilst, with a larger quantity, the acetic acid would be liquid instead of crystallized; and for this reason the common concentrated sulphuric acid, which contains more than one atom of water, cannot be employed. The process is thus expressed:

1 at. $PbO + \bar{A}$, and 1 at. $SO_3 + HO$, form
1 at. $PbO + SO_3$, and 1 at. $\bar{A} + HO$.

For 2370 parts (crystallized) of acetate of lead, 613 parts of sulphuric acid would suffice; but to im-

part a certain fluidity to the mixture, a larger portion of sulphuric acid is used. As soon as the acid comes in contact with the salt of lead, a considerable rise of temperature takes place, which would cause a fracture of the retort, if the latter were not previously warmed, and the acid added in small portions at a time. The double bend in the funnel tube serves to hold a small quantity of sulphuric acid, and this prevents the escape of the acetic acid vapours.

The distillate always contains sulphurous acid, and probably a trace of lead and sulphuric acid; the two latter are mechanically carried over by the violence with which the acetic acid fumes are evolved. The sulphurous acid is partly present in the fuming sulphuric acid, and partly arises from the decomposition of the latter into sulphurous acid and oxygen. The affinity of the concentrated sulphuric acid for water is so great, that if none is present it forms it from its elements, and as these elements are obtained from a portion of the acetic acid, the carbon of this substance is liberated, and some of it deoxidizing another part of the sulphuric acid causes the evolution of carbonic and sulphurous acids. For this reason the residue in the retort is never white, but of a brown colour, from the free carbon. In order to remove these impurities, we have recourse to the peroxide of manganese ($=MnO_2$), which, furnishing oxygen to the sulphurous acid, converts it into sulphuric and hyposulphuric acids; these enter into combination with the protoxide of manganese that remains, and of course, on rectification, are left behind with the lead and sulphuric acid that may have been present.

When common acetate of soda is used, the presence of the extractive matter is another cause of the formation of sulphurous acid, (as explained in the previous article).

Properties.—Hydrated acetic acid forms a mass of colourless crystalline plates, of a very penetrating smell and sour taste; it melts between 55° and 61° Fah., and then forms a colourless liquid having a specific gravity of 1·063. Exposed to the air it fumes, from the abstraction and condensation of the vapours of water contained in the atmosphere, gradually loses its crystalline property and becomes liquid. Its ordinary impurities, *lead*, *sulphuric* and *sulphurous acids*, may be detected as in concentrated acetic acid.

ACIDUM ARSENICUM.

Arsenic Acid.

FORMULA: As_2O_5.

Preparation.—4 Parts of arsenious acid (white arsenic) are coarsely powdered in an iron mortar, then transferred to a porcelain one and rubbed to a fine powder (a little alcohol being added to allay the dust), then gently warmed to drive off the spirit, and put into a retort with 12 parts of nitric acid, of 1·2 spec. grav. After a receiver has been adapted, which must closely fit the neck of the retort, it is heated in a sand bath so long as anything goes over. The heat of the sand bath is sufficient to expel all the nitric acid. In order to remove the dry arsenic acid, the retort must be broken; but should this not be desired, 10 parts of water may be added and the retort heated in a sand bath until all its contents are dissolved; then pour into a porcelain dish and evaporate to dryness. The produce will be nearly 5 parts.

Recapitulation.—Arsenious acid consists of 2 at. of arsenic ($=As_2$), and 3 at. of oxygen (O_3), $=As_2O_3$; the nitric acid of 1 at. of nitrogen (N) and 5 at. oxygen (O_5), $=NO_5$. 3 At. arsenious acid abstract

from 2 at. of nitric acid 6 at. of oxygen, and form 3 at. arsenic acid, $=As_2O_5$; the nitric acid being reduced to nitric oxide, NO_2. This last would be given off as a colourless gas; but its affinity for oxygen is so great, that it abstracts it from the atmospheric air contained in the apparatus, and hyponitric acid $=NO_4$ (nitric and nitrous acids $=NO_5+NO_3$) is formed, which passes into the receiver as yellowish brown vapour, and becomes absorbed by the water that has distilled from the nitric acid.

3 at. As_2O_3, and 2 at. NO_5 form
3 at. As_2O_5 2 at. NO_2; and this last, with
4 at. O, forms 2 at. NO_4.

The quantity of nitric acid requisite, according to stochiometrical calculations, is not in practice sufficient to convert the whole of the arsenious acid into arsenic acid, as a portion of it distils over unchanged with the products of decomposition. An excess of nitric acid must therefore be employed, and the above proportions (4 parts of arsenious acid and 12 parts of nitric acid, containing 73 per ct. of water) correspond to 3 at. As_2O_3, and 4 at. NO_5. On account of the possibility of its containing a small portion of arsenic, the distillate must be used for no other purpose.

Properties.—Prepared as just directed, arsenic acid is a white porous mass. It must entirely volatilize at a red heat, being first decomposed into oxygen and arsenious acid. It is soluble in two parts of water. The presence of *nitric acid* (occurring when the distillation is discontinued too soon) may be detected by the decolorization of a drop of solution of indigo when added to a concentrated solution of the arsenic acid in water. Or a small portion is placed in a narrow test tube, a few copper filings and water are added and gently warmed; if nitric acid be present, the tube will be filled with yel-

lowish brown vapours, which arise from the oxidation of the copper by the nitric acid; the latter being reduced to nitric oxide, then instantly abstracting oxygen from the air, it becomes hyponitric acid. The oxide of copper combines with the arsenic acid.

6 at. Cu, 2 at. NO_5, and 3 at. As_2O_5, form
3 at. $2CuO + As_2O_3$, and 2 at. NO_2; these last, with 4 at. O, form 2 at. NO_4.

With nitrate of silver the arsenic acid gives a brownish red precipitate of arseniate of silver: if it approaches a yellow colour it proves that it still contains *arsenious acid*. This is determined with greater certainty by sulphuretted hydrogen, which is passed into a solution of 1 part of arsenic acid dissolved in 50 parts of water, containing a little hydrochloric acid. In case arsenious acid is present, a lemon yellow precipitate of golden orpiment (As_2S_3) is formed; the hydrogen of the sulphuretted hydrogen and the oxygen of the arsenious acid combine as water, whilst the sulphur unites with the arsenic. It is necessary that the solution be dilute, in order to avoid the decomposition of the arsenic acid, which would form a pale yellow precipitate of the higher sulphuret, As_2S_5; the hydrochloric acid is added to facilitate the separation of the sulphuret of arsenic.

ACIDUM BENZOICUM.

Flores Benzoes. Benzoic Acid. Flowers of Benjamin.

Formula: $C_{14}H_5O_3 + HO = \overline{B} + HO$.

Preparation.—This acid may be obtained from gum benzoin either by the dry or wet method. By the wet method it is obtained in a larger quantity, and sufficiently pure for medicinal purposes; nevertheless, should a perfectly white salt be desired,

this is only obtained at the expense of the produce, and the dry method must be resorted to.

(*a*) *By the dry method.*—A layer of powdered gum benzoin, not more than $\frac{1}{2}$ an inch thick, is spread over the surface of a flat earthen dish with a raised rim, on which a sheet of white bibulrus paper is strained and pasted; over this is affixed a conical-shaped cap of glazed paper, with a diameter somewhat larger than the edge of the dish; and the apparatus thus prepared is placed on the iron plate of a stove, in which a gentle fire is kept up, which may afterwards be somewhat increased, but not sufficiently to allow the resin to char, as the products of decomposition would in this case contaminate the sublimed benzoic acid. From time to time the paper cap is taken off, and its contents, as well as the crystals on the filtering paper, brushed off into a proper vessel. When no more sublimate is formed the process is ended. The product is from $\frac{1}{12}$ to $\frac{1}{16}$ of the resin taken.

(*b*) *By the wet method.*—8 Parts of powdered gum benzoin are mixed with 2 parts of hydrate of lime in a glass flask, well shaken together, and so much water added that the whole forms a thin paste (for which purpose 16 parts of water suffice); the flask is then placed in a sand bath for 24 hours, frequently shaken, and the water renewed so often as it evaporates. Where several pounds of resin are operated on at once, a copper vessel is more serviceable. The pasty mass is transferred to a copper vessel, 100 parts of water added, and, being constantly stirred with a wooden spatula, the whole is boiled until about 30 parts of water have evaporated; whilst still hot it is filtered through white blotting paper spread on linen; the residue is again boiled with 50 parts of water, and the two filtered solutions mixed and evaporated to 32 parts; with constant stirring, hydrochloric acid is now added so long as it causes a turbidness (2 parts of an acid

of spec. grav. 1·130 are sufficient), and the whole allowed to remain undisturbed in a cool spot for a day or two. After this time we shall find it all changed into a thick crystalline paste. The benzoic acid is now separated from the solution by a linen strainer, well pressed and dried, then boiled with twenty times its weight of water; when dissolved, it is strained through linen and allowed to stand a day or two; the crystals are then separated, pressed, and dried for use. 8 Parts of gum benzoin should yield, by this process, 1 or 1½ parts of acid.

The acid is generally prepared in the wet way by treating the resin with a solution of carbonate of potash or soda; the disadvantage of this method is the loss of product, as, when the solution is heated, the gum agglutinates and prevents the action of the alkali. With lime, on the other hand, this is obviated, as the resin always remains, during the boiling, in a state of powder.

Recapitulation.—The benzoic acid exists in a free state in the resin, and will therefore, on account of its volatility, be expelled by heating, though a certain portion is always lost in this process, owing to its decomposition (at the expense of other constituents of the gum benzoin). By treating with lime, this simply combines with the acid, forming the readily soluble benzoate of lime, which is again decomposed by the hydrochloric acid, the benzoic acid separating as a fine crystalline powder, whilst the chloride of calcium formed remains in solution. The object of the subsequent solution in hot water is to effect the separation of resin, which has become dissolved in the treatment with lime. The mother liquors from which the acid has separated, not being worth evaporating, may be thrown away. The residuary resin, after sublimation, may be used in fumigating mixtures, if it has not been too strongly heated, that is to say charred.

Properties.—The sublimed acid forms groups of

needles and scales, exceedingly light, of a brilliant white satin-like lustre; that prepared by boiling appears as pale yellow needles. The scent reminds one of gum benzoin, and is due to a volatile oil which adheres to the crystals. When heated in a platinum spoon it fuses and is entirely converted into a white vapour, which, when inhaled, causes a peculiar pricking sensation in the throat. It is readily soluble in spirits of wine, but difficultly so in water, of which, when cold, it requires 200, when boiling 20 parts for its solution. The commercial acid is sometimes adulterated. If it is volatile and, when treated with solution of potash, evolves ammonia, *sal ammoniac* is present; the potassium combines with the chlorine of the sal ammoniac, and the ammonia is liberated. If a residue occurs on heating, it consists of some foreign substance, as *gypsum*, *boracic acid*, or any other salt, the nature of which must be determined by further experiments. Should the residue be carbonaceous, it may arise from the presence of *resin*, or the salt of some *organic acid*. If the acid has the odour of the sweat of a horse, it consists entirely or partly of that nitrogenized acid found in the urine of herbivorous animals, viz. *hippuric acid*; and in this case, when mixed with lime and heated in a glass tube, ammonia is evolved, the nitrogen combining with a portion of the hydrogen. Should no ammonia escape in this experiment, it will contain no hippuric acid, but has probably been prepared from it, and the odour not entirely removed.

ACIDUM BORACICUM.

Sal seditivus Hombergis.—Boracic Acid.

Formula: $BO_3 + 3HO$.

Preparation.—4 Parts of powdered borax are put into a glass or porcelain vessel, with 10 parts of

water, and heated to boiling; when dissolved, the solution is filtered, mixed with three parts of hydrochloric acid, spec. grav. 1·130, and allowed to cool. The crystalline scales begin to form immediately; they are collected, after a day or two, on a funnel, the neck of which is loosely stopped with a glass stopper, and allowed to drain; after most of the mother liquor has separated, they are slightly pressed together, washed with a little distilled water, and dried. They are then dissolved in six times their weight of boiling distilled water, allowed to crystallize, drained as before, and dried. The produce will be about 1½ parts.

If the borax be decomposed with sulphuric acid, as generally recommended, the boracic acid will contain a small portion of sulphuric acid, that can be separated only by alcohol, or by heating to redness.

Recapitulation. — Borax consists of 1 at. soda (NaO), 2 at. boracic acid (BO_3), and 10 at. water (HO), $=NaO + 2\,BO_3 + 10\,HO$; the hydrochloric acid of 1 at. chlorine (Cl), and 1 at. hydrogen (H). The sodium, on account of its greater affinity for chlorine, unites with it, forming chloride of sodium; the oxygen of the soda forms water with the hydrogen of the hydrochloric acid; and the greater part of the boracic acid, combined with 3 at. of water, separates, being only slightly soluble in water. To decompose 1 at. of borax exactly 1 at. of hydrochloric acid is necessary.

1 at. $NaO + 2BO_3 + 10HO$, and 1 at. ClH, form
1 at. NaCl, 2 at. $BO_3 + 3HO$, and 5 at. HO.

2387 Parts of borax require 455 parts of anhydrous or 1750 parts of hydrochloric acid, of spec. grav. 1·130 (which contains 26 per ct. of anhydrous acid); consequently 4 parts of borax require 3 parts of this hydrochloric acid. A slight excess of the latter is not disadvantageous, as it insures the total

decomposition of the borax, and is all dissipated on drying. The recrystallization of the acid is to remove a slight trace of chloride of sodium. 4 Parts of borax should yield exactly 2 parts of acid; a portion, however, remains in the mother liquor, which, when operating on small quantities, may be thrown away, but on the large scale is evaporated and the acid saved.

Properties.—Boracic acid forms white scaly crystals, of a mother-of-pearl lustre, feeling unctuous to the touch, having no smell, and a feebly-sour, somewhat bitter taste. In the heat it loses water, fusing to a colourless glass, which remains transparent on cooling. The crystallized acid dissolves in 25 parts of water and 6 of alcohol, at the ordinary temperature; but requires only 3 parts of boiling water for its solution. The solutions either redden litmus paper or colour turmeric paper brown, according to their concentration. In spirits of wine it burns with a green flame. When not carefully prepared, *chloride* of *sodium* may be present, and nitrate of silver will cause a white casiform precipitate of chloride of silver, becoming violet in the light, whilst at the same time nitrate of soda is formed. If the materials used contained *sulphur*, or should sulphuric instead of hydrochloric acid have been used, *sulphuric acid* is always present, and nitrate of baryta will cause a white precipitate of sulphate of baryta, insoluble in nitric acid. If the acid has a yellow colour (as is easily the case when the common acid from Tuscany is purified), either *iron* or *organic matter* is present. The latter is known by the acid becoming black when heated in a platinum spoon. When iron is present, it is separated by repeated solutions in hot water, as hydrated oxide of iron, and the solution gives, with tincture of galls, a violet or blue precipitate of tanno-gallate of iron (the base of our writing ink).

ACIDUM FORMICUM.

Formic Acid.

FORMULA : $C_2HO_3 + xHO = \bar{F} + xHO$.

Preparation.—3 Parts of white sugar are dissolved in 6 parts of water, and the solution poured into a copper still, which is sufficiently large to hold at least 5 times as much as the quantity of substance used; to this is added 9 parts of finely-powdered peroxide of manganese, the whole warmed by means of a charcoal fire, to about 140 Fah., and a mixture of 9 parts of strong sulphuric acid, and 9 parts of water added, in small portions at a time on account of the strong frothing up it occasions. The still should be connected with a tube, through which the sulphuric acid can be poured, so that as soon as the smell of formic acid is evolved, the head may be fixed on and luted. When all is added, the fire is increased, and the distillation carried on to dryness. The milky distillate, on which a thin layer of a brownish yellow ethereal oil swims, is saturated with crystallized carbonate of soda, of which about 2 parts will be necessary, filtered and evaporated to dryness. About 2 parts of yellow formiate of soda are obtained; and the pure formic acid, by distilling this with sulphuric acid.

The relation between formiate of soda and concentrated sulphuric acid is 1 at. or 1 part (14 parts) of the former, and 2 at. $1\frac{3}{7}$ parts (20 parts) of the latter. The salt is placed in a retort large enough to hold twice the quantity; to this, the sulphuric acid, first mixed with its own weight of water, is added, and, after connecting with a receiver, the retort is heated and the distillation continued until the contents, which gradually become dark, commence puffing up. 2 Parts of formiate of soda yield 4 parts of acid of a spec. grav. 1·074.

Instead of sugar, starch may be employed; so also carbonate of lime may replace carbonate of soda in neutralizing. One part of dry formiate of lime requires $\frac{3}{4}$ of its weight of concentrated, or an equivalent quantity of diluted, suphuric acid.

Recapitulation.—White sugar, both cane and beet-root sugar, consists of $C_{12}H_{11}O_{11} = C_{12}H_{10}O_{10} + HO$; black oxide of manganese, apart from the impurities which it always contains, as iron, chalk, &c., is nearly a peroxide, consisting of 1 at. manganese (Mn) and 2 at. oxygen $(O_2) = MnO_2$; or, 1 at. protoxide of manganese (MnO) and 1 at. $(O) = MnO + O$. When the sulphuric acid comes in contact, it seizes the protoxide of manganese, whilst the oxygen of the peroxide becoming liberated, oxidizes the sugar, and forms with it nothing but volatile products, viz., carbonic acid, $= CO_2$; formic acid, $= C_2HO_3$; an ethereal volatile oil, $= C_5H_2O_2$; and water, HO. No investigation has hitherto been carried out as to the relative proportion of the volatile matters obtained from a given quantity of sugar. It is impossible, therefore, to give a stochiometrical formula of the process. By employing starch $(C_{12}H_{10}O_{10})$ exactly the same products are obtained.

The sulphate of manganese remaining in the still, is purified, if required for use, by heating to low redness in a Hessian crucible (in order to destroy the organic matter, and render the iron insoluble), then dissolved, filtered, and crystallized.

The preparation of the formic acid from the soda or lime salt is based on the stronger affinity of sulphuric acid to those bases; forming either bi-sulphate of soda or neutral sulphate of lime. The sulphuric acid must not be used concentrated, as it would decompose the formic acid into carbonic oxide and water. From 1 at. C_2HO_3 are formed, under these circumstances, 2CO and HO.

Properties.—Pure formic acid is a colourless liquid, of a sour taste and sharp pungent smell, something

like acetic acid. It is miscible with water, spirit, and ether, in all proportions, without forming a turbid solution. The acid of a spec. grav. 1·074 contains 79 per ct. or 15 at. of water. In order to determine whether *acetic acid* is present, and prepared as above directed this is often the case, a small portion is diluted with water, boiled with excess of peroxide of mercury, and filtered as soon as the effervescence ceases. If one portion of the filtered solution gives a black precipitate with sulphuretted hydrogen, and another portion, when gently evaporated, yields feathery or white scaly crystals, the presence of acetic acid is demonstrated. In this reaction the formic acid abstracts oxygen from the peroxide of mercury, reducing it to the protoxide with the necessary quantity of which, acetic acid, if present, combines to form the soluble (though difficultly so in the cold) proto-acetate of mercury ($Hg_2O + \bar{A}$). The remainder of the protoxide, even when excess of peroxide is present, will be reduced to the metallic state by the formic acid, with evolution of carbonic acid :—

2 at. HgO and 1 at. C_2HO_3, form
2 at. CO_2, 1 at. HO, and 2 at. Hg,

whilst the acetate of mercury that is formed remains in solution unchanged. This latter salt is readily known by the form of its crystals and decomposition by sulphuretted hydrogen into free acetic acid and sulphuret of mercury :—

1 at. $Hg_2O + \bar{A}$ and 1 at. SH, form
1 at. Hg_2S, HO, and $\bar{A}$.

Hydrochloric acid is known by the white casiform precipitate with nitrate of silver, and *sulphuric acid* by the white pulverulent precipitate with nitrate of baryta.

Purification.—If the formic acid be coloured yellow, it is to be rectified over powdered charcoal. If

it contain hydrochloric or sulphuric acid, a little carbonate of soda is added, (as much as appears necessary to neutralize these two acids,) and then distilled nearly to dryness. If it contain acetic acid it will be necessary to saturate the acid with carbonate of lead, and then to separate by filtration the difficultly soluble formiate of lead from the readily soluble acetate. The precipitate is dried and distilled with $\frac{1}{3}$ its weight of concentrated sulphuric acid, previously diluted with an equal weight of water.

ACIDUM GALLICUM.

Gallic Acid.

FORMULA: $C_7HO_3 + 2HO + Aq = \bar{G}a + 2HO + Aq$.

Preparation.—Any quantity of finely powdered gall nuts is mixed, in a shallow porcelain or glazed vessel, with sufficient water to form a thin paste. The mass is frequently stirred, the water renewed as it evaporates, and allowed to stand several months, until the filtered solution of a portion, previously mixed with water, gives no precipitate with a solution of gelatine; in the summer the ordinary temperature is sufficient, but in the winter it will be necessary to place it near a fire. If on testing with gelatine solution, only a slight turbidness ensues, this will not be of consequence, as the tannic acid present will eventually remain in the mother liquid. The mass is now mixed with at least 8 times its weight of water, boiled for half-an-hour, the gray or blackish solution strained through a thick linen cloth, and the residue well washed with hot water. The whole of the filtered liquids are now evaporated in the same porcelain vessel, previously cleaned, until of the thickness of syrup; then mixed with finely powdered wood charcoal, (about $\frac{1}{4}$ of the

weight of the gall nuts employed,) and carefully evaporated to dryness. The dried mass is powdered and digested in the sand bath with four times its weight of alcohol, of at least 80 per ct., filtered whilst warm, and again digested with the same quantity of alcohol; the yellow spirituous solutions are mixed with some water, and then distilled from a retort, in order to recover the alcohol. The crystalline pasty mass is rinsed out into a dish, and so much water added, that on heating it forms a solution, which is to be quickly filtered and placed in the cold. After several days the crystalline mass is pressed, (the mother liquor on evaporation yields some acid,) and purified by dissolving several times in hot water and crystallizing. The produce is somewhat more than a third of the weight of the galls used.

The method employed by Scheele, the discoverer of gallic acid, viz., to allow an infusion of gall nuts to become mouldy, is both more tedious and less productive. The same may be said of the process by treating an infusion of gall nuts with sulphuric or hydrochloric acid.

Recapitulation—Gallic acid does not exist in gall nuts ready formed, but is produced, together with carbonic acid, by the action of the atmospheric oxygen on the tannin, of which the gall nuts contain variable proportions according to their goodness, but generally more than 50 per ct.; 1 at. of tannin absorbs 8 at. of oxygen, and forms 2 at. of gallic acid, 6 at. water, and 4 at. carbonic acid :—

1 at. $C_{18}H_8O_{12}$ and 8 at. O, form
2 at. C_7HO_3, 6 at. HO, and 4 at CO_2.

2650 Parts of tannin must, therefore, form 1688 parts of anhydrous gallic acid, or 2363 of crystallized, combined with 3 at. of water. So much as this is, however, never obtained in practice, because during the digestion of the gall nuts with water, a portion of the first-formed gallic acid becomes con-

verted into a gray or black carbonaceous body. To separate this entirely, the watery extract must be treated with alcohol, in which this foreign body is insoluble, and the charcoal powder is added in order to dry and powder the extract more readily. The latter also serves to decolorize the product.

Properties.—Pure gallic acid crystallizes in white needles, which entirely sublime when heated, but it then possesses another composition being the so-called *pyro-gallic* acid, which is crystallized gallic acid, minus 1 at. water and 1 at. carbonic acid $= C_6H_3O_3$.

1 at. $C_7HO_3 + 2HO + Aq.$, forms
1 at. $C_6H_3O_3$, 1 at. CO_2, and 1 at. HO.

Gallic acid is odourless, tastes slightly acid and astringent; it dissolves in 100 parts of cold, but much more readily in hot water, as well as alcohol; it is also tolerably soluble in ether. If it contains any *tannin* a solution of gelatine is rendered turbid by it, whilst pure gallic acid should effect no change. This precipitate or turbidness consists of a compound of tannin and gelatine, which is insoluble in water, in fact leather is formed; the manufacture of this precipitate on the large scale constitutes the important art of tanning.

ACIDUM HYDROCYANICUM.

Prussic Acid.—Hydrocyanic Acid.

FORMULA: $HCy\ (HC_2N) + xHO$.

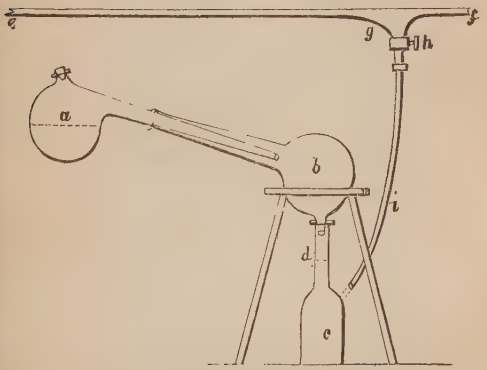
Preparation.—Hitherto the ferrocyanide of potassium has almost always been used for the preparation of prussic acid; as, however, we have for some time been acquainted with a cheap and easy method of preparing cyanide of potassium, we may expect that it will finally replace the ferrocyanide, the use

of which is attended with some inconvenience in the manufacture of the acid; both methods will here be fully discussed.

(*a*) *From Ferrocyanide of Potassium.*—Of the many processes that have been described, I will mention only one, which yields a preparation remaining unaltered for twelve months, according to my own experience. It is the same as contained in the "Bavarian Pharmacopœia." 4 Parts (ounces) of ferrocyanide of potassium (yellow prussiate of potash) are dissolved in 16 parts of common water, in a stoppered glass bottle, a previously cooled mixture of 3 parts concentrated sulphuric acid and 12 parts alcohol, spec. grav. 0·84 (=80 per ct.), is added, and allowed to digest, with occasional shaking, for 24 hours, at the ordinary temperature. The crystalline sediment is then separated by a linen strainer, the liquid placed in a tubulated retort, capable of holding at least 6 times as much, at the bottom of which is a layer of silver sand, and then, either over a naked fire or sand bath, so much is distilled from it as will equal in bulk 20 parts of distilled water. The weight of this distillate will equal 18½ parts; and if we consider 20 parts of distilled water as 20 ounces, the like volume of the distillate will weigh 18½ ounces. To determine this quantity exactly (for it must not be distilled to dryness) the apparatus should be constructed as in the accompanying wood-cut.

To the retort (*a*), which is so placed that its neck is inclined as slightly as possible, is attached by means of airtight bladder, the tubulated receiver (*b*) in such a manner that the exit tube, which must be as long and as fine as possible, points downwards. The receiver itself rests on a stool, having a circular hole in the middle, of some inches diameter, through which this tube passes. The tube is connected with a bottle, having a neck sufficiently large to allow it to be inserted, and capable of holding somewhat

more than 20 ounces of water. The most convenient sort of bottle is one, as *c*, having a long neck, to about the middle of which 20 ounces of water will reach; this point is marked with a file, the water emptied out, the bottle and tube connected with bladder, having a few small holes punctured in it, to permit the air, which becomes expanded during the distillation, to escape. A stream of water is allowed to flow on the bottle to cool it, and



not on the receiver, as otherwise the bladder would become softened and permeable. With the refrigeratory apparatus in use in the laboratory of the Pharmaceutical Institution at Munich, this is especially easy. To the wall of the chimney is attached a thick leaded pipe (*e f*), in which, at a distance of $1\frac{1}{2}$ feet, are soldered perpendicular exit pipes (*g*), at the other ends of these are straight brass taps (*h*). Over the tube of the cock is passed a leathern hose or pipe, of about $\frac{1}{2}$ an inch in diameter; this is fastened with pack-thread, and the other end con-

ducted to the receiver. The quantity of water that passes may be regulated by the tap. So soon as the product of distillation reaches the neck, the bottle is taken away, and a fresh one substituted; or else the apparatus should be removed into the open air, to prevent any ill effects happening to the manipulator from the hydrocyanic acid vapours which yet continue to be evolved from the retort.

(*b*) *From Cyanide of Potassium, prepared according to Liebig's method.*—The apparatus just described may be used in this case, but if only one or two ounces are to be prepared, which, for medicinal purposes, is often most convenient, the following

method is more simple. In a glass flask (*a*), holding from 4 to 6 ounces, is fitted a well-closed cork, through which is passed the shorter limb of a doubly-turned glass tube, or rather of two glass tubes, bent at right angles, and fastened together; the longest limb dips into a glass bottle (*b*), which, to a certain point in the neck (that is marked with a file) will hold 1080 grains of distilled water. In this (empty) glass bottle 660 grains of alcohol, spec. grav. ·840, are weighed; in the flask 810 grains of dilute sulphuric acid (consisting of one part strong acid and 5 parts water) are poured, and to this are added 135 grains of cyanide of potassium, if possible in

one piece, the cork quickly inserted, then luted and secured with bladder, the longer limb of the tube is passed into the bottle below the surface of the alcohol, and the mouth of the bottle tied over with bladder, which is then punctured with a pin. The flask is now heated on a sand bath until the bottle (which must be kept very cool) is full up to the file mark, on which the tube is immediately withdrawn, and the bottle corked. The distillate, which, with the alcohol, occupies the space of 1080 grains of distilled water, will weigh exactly 1000 grains.

Recapitulation (*a*).—The yellow prussiate of potash is a compound of 2 at. cyanide of potassium, 1 at. of protocyanide of iron, and 3 at. of water = 2KCy + FeCy + 3HO. When brought in contact with dilute sulphuric acid, only $\frac{2}{3}$ of the cyanide of potassium form hydrocyanic acid and potash, water being evolved; the remaining $\frac{1}{3}$ of the cyanide of potassium escapes decomposition, and combined with the cyanide of iron, remains in solution. If we take, in order to avoid fractions, 3 at. of yellow prussiate of potash, the process is explained by the formula, as follows:—

3 at. 2KCy + FeCy + 3HO, and 4 at. SO_3 + HO, form 1 at. 2KCy + 3FeCy, 4 at. KO + SO_3 and 4 at HCy.

7926 Parts of the yellow salt require 2452 parts of hydrated sulphuric acid. The prescribed quantity of acid (3 parts to 4 of the salt) is consequently more than sufficient to form the bi-sulphate of potash; the excess is of no consequence. If we assume that bi-sulphate of potash is formed, this, as soon as alcohol is introduced, will be converted into free sulphuric acid and sulphate of potash. The white crystalline precipitate that occurs on mixing sulphuric acid and alcohol to a solution of prussiate of potash, consists of the sulphate of potash. The separation of the sulphate of potash, previous to distillation, is not, however, the most

important service the alcohol renders; its chief use is to preserve the prussic acid. Without the addition of alcohol, the prussic acid soon begins to decompose, becoming of a brown colour, and cyanide of ammonium is formed, whilst a carbonaceous substance, containing nitrogen, subsides :—

4 at. HCy form
1 at. NH_4Cy and $Cy_2 + C_2$.

During the distillation of the alcoholic solution, after its separation from the sulphate of potash, a white deposit forms, which gradually becomes green, then blue, and, by adhering to the bottom of the retort, occasions a strong bumping of the contents, often causing a portion to spirt over, or even the fracture of the retort; to avoid this, a little silver sand is placed in the retort, which prevents the precipitate from lying too closely at the bottom. Platinum wire, which has been recommended, does not effect this. The decomposition of the compound $2KCy + 3FeCy$ during the distillation, is the cause of the precipitate, which consists of cyanide of iron FeCy; this, however, is not quite pure, but combined with a certain portion of cyanide of potassium. The change of colour in the precipitate, which finally becomes blue, is due to the formation of prussian blue ($3FeCy + 2F_2Cy_3$); this is caused by the action of the oxygen of the air on the FeCy, which first forms protoxide, and afterwards peroxide of iron :—

9 at. FeCy and 3 at. O form
1 at. $3FeCy + 2Fe_2Cy_3$ and 1 at. Fe_2O_3.

If we trace the decomposition of the substance $2KCy + 3FeCy$ more exactly, we shall find that so soon as cyanide of iron, containing but little cyanide of potassium precipitates, cyanide of iron richer in cyanide of potassium, must remain in solution,—that is, some yellow ferrocyanide of

potassium ($2KCy + FeCy$) is instantly formed; on this the free sulphuric acid present will act as at first (when the solution of yellow prussiate of potash is brought in contact with the alcohol and sulphuric acid); at the same time the fresh quantity of prussic acid evolved is so trifling as not to affect the preceding assumption, that only $\frac{2}{3}$ of the cyanide of potassium present in the ferrocyanide of potassium is converted into prussic acid; this the following observation proves:—

4 ounces of crystallized ferrocyanide of potassium contain 708 grains of cyanogen, of which $\frac{2}{3} = 472$ grains, belong to the potassium, and $\frac{1}{3}$, $= 236$ grains, to the iron. The distillate ($18\frac{1}{2}$ ounces) contains ($3\frac{1}{2}$ per ct., or) 311 grains of anhydrous prussic acid, which denotes 300 grains of cyanogen. $472 \times 2{:}3$ however $= 315$ grains. The deficiency of 15 grains ($315 - 300 = 15$) in the distillate is compensated for by an exact attention to the direction, according to which only so much shall be abstracted as will occupy the space of 20 ounces of water. The small quantity of liquid remaining in the retort indicates, however, by its smell, the presence of a little prussic acid; and finally it must not be forgotten, that it is almost impossible to avoid a trifling loss of the acid during the process.

(*b*) Fused cyanide of potassium consists of 7 at. cyanide of potassium (K.Cy) and 3 at. of cyanate of potash ($KO + CyO$) $= 7KCy + 3\ (KO + CyO)$.* By sulphuric acid and water it is decomposed, so that the cyanide of potassium is converted into hydrocyanic acid and potash, which, combining with the sulphuric acid, forms sulphate of potash. The potash of the cyanate of potash at the same time passes to the sulphuric acid, whilst the

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* The formula here given for the fused cyanide of potassium, is based on several of my own analyses of this salt, which will be noticed under the article Kali cyanatum fusum.

liberated cyanic acid, owing to the water present, is converted into carbonic acid and ammonia; the former of these is evolved, and the latter combines with the sulphuric acid. The residue of the distillation is consequently sulphate of potash and sulphate of ammonia; whilst prussic acid, carbonic acid, and water are given off.

1 at. $7KCy + 3(KO + CyO)$, 13 at. SO_3 and 19 at. HO, form
10 at. $KO + SO_3$, 3 at. $NH_4O + SO_3$, 7 at. HCy, and 6 at. CO_2.

8750 Parts of cyanide of potassium require, according to this, 7969 parts of hydrated sulphuric acid. Equal parts of both is the best proportion, as the small excess of sulphuric acid assists in the decomposition. 135 Grains of cyanide of potassium contain 35·1 grains cyanogen capable of forming cyanide of hydrogen; the quantity of the latter, that is of anhydrous prussic acid, equals therefore 36·2 grains. On account of a small loss, which is unavoidable, the distillate mixed with the alcohol, that is 1000 grains, will not contain more than 35 grains. Consequently 100 grains contain 3·5 grains, or 3½ per ct., and the strength of this prussic acid corresponds with that prepared from prussiate of potash, described under (*a*). The same quantity of alcohol is also contained in each, viz. 52 per ct. by weight, the spec. grav. is ·900, so that both the prussic acids are in every respect identical. An insignificant objection to the identity of the two acids is, that by the action of sulphuric acid on the alcohol ether is formed, and the presence of formic acid has been noticed.

According to the proportion of cyanide of potassium, the prussic acid will be stronger or weaker. For instance, 116 grains cyanide of potassium (with the same quantity of sulphuric acid, alcohol, &c., as for 135 grains of cyanide of potassium) will

give an acid of 3 per ct., 77 grains one of 2 per ct., and so on.

Properties.—Prepared according to either method, the prussic acid is a colourless, highly-poisonous fluid, smelling strongly of bitter almonds and alcohol, has a spec. grav. of 0·900, and is entirely volatile. In order to prevent, as much as possible, any decomposition or change in strength, it should be kept in a well-closed bottle, in a cool and dark place. The proportion of anhydrous prussic acid may be determined either by oxide of mercury or nitrate of silver.

1. *Treatment with Oxide of Mercury.*—100 Grains of prussic acid are diluted with 200 grains of water, introduced, with a weighed portion of oxide of mercury, into a well-closed bottle and allowed to digest, being frequently shaken, for 2 days. If at the expiration of this time all the oxide is dissolved, another weighed portion must be added, and the shaking repeated 2 days longer. The undissolved portion is now collected on a weighed filter, well washed with water, dried and weighed; on deducting the weight of the filter from the oxide of mercury, the quantity dissolved is learned; this divided by 4 gives the quantity of anhydrous prussic acid in 100 grains. For instance, 20 grains of oxide are employed, and 6 grains remain undissolved, thus $14 \div 4 = 3\frac{1}{2}$ per ct. of anhydrous acid. The theory of this proceeding is as follows:—when oxide of mercury is dissolved in prussic acid, cyanide of mercury and water are formed.

1 at. HgO, and 1 at. HCy, form
1 at. HgCy, and 1 at. HO.

1350 Parts of oxide of mercury combine with 338 parts of cyanide of hydrogen, or 4 parts (338 × 4) of the first with 1 part of the latter.

2. *Testing with Nitrate of Silver.*—100 Grains of prussic acid are diluted with 2000 grains of water,

and a solution of nitrate of silver added as long as a precipitate ensues. When entirely separated, the white precipitate is collected on a weighed filter; its weight (the filter of course being deducted) divided by 5 gives the amount of anhydrous prussic acid.

1 at. $AgO + NO_5$, and 1 at. HCy, form
1 at. AgCy, 1 at. HO, and 1 at. NO_5.

1675 Parts of cyanide of silver correspond to 338 parts of hydrocyanic acid, or 5 parts (338×5) of the first to one of the latter. The precipitated cyanide of silver divided by 5 does not give quite so correct a result as the dissolved oxide of mercury divided by 4, as in the former the quotient ($1675 \div 5$) is 335.

As impurities, the prussic acid may contain—*sulphuric acid*, when from a carelessness in distillation some has spirted over; nitrate of baryta then gives a white insoluble precipitate. From the same cause the distillate, when ferrocyanide of potassium is employed, contains *prussian blue;* this, on standing, is deposited in pale blue flakes. In this latter case it must of necessity contain *potash*. *Hydrochloric acid* will occur from the use of a salt containing chloride of potassium; in order to detect this acid with certainty, it is better to get rid of the prussic acid. Some borax (free from chloride) is added to the acid, and the latter evaporated to dryness by a gentle heat, the residue, dissolved in water, is treated with excess of nitric acid, and a few drops of nitrate of silver solution added; a white precipitate, becoming violet in the light, consists of chloride of silver. In this case the hydrochloric acid decomposes the borax (*Vide* ACIDUM BORACICUM), chloride of sodium is formed, and the prussic acid evaporates. Instead of borax pure carbonate of lime may be employed, which is not decomposed by prussic acid; or, the acid is super-

saturated with ammonia and carefully evaporated to dryness; if there be no residue the acid is pure; but, on the contrary, a saline mass, soluble in water, giving, on the addition of nitrate of silver, chloride of silver, denotes the presence of chlorides. In this case the cyanide of ammonium, which is formed on saturating the acid, is so volatile as to be dissipated with the vapour of the water, which does not happen with chloride of ammonium. It is difficult to prevent the occasional formation of formic acid in the manufacture of prussic acid; this is, however, of little consequence; in order to discover it, the distillate is treated with oxide of mercury, which will be reduced by the formic acid; (*Vide* ACIDUM FORMICUM).

ACIDUM HYDROFLUORICUM.

Hydrofluoric Acid.

FORMULA: $HF + xHO$.

Preparation. — 1 Part of finely-powdered fluor spar is supersaturated in a platinum, or leaden bottle, with 3 parts of concentrated sulphuric acid, and well mixed together with a platinum or leaden rod. A tube, of the same metal, bent at right angles, is now affixed to the mouth of the bottle, well luted, and the other end tightly fitted into a platinum or leaden receiver. When all the joints have been well luted and fastened, the vessel containing the substance is to be gently warmed, on which thick white vapours are formed and pass over into the (well-cooled) receiver as drops of liquid. After warming from ½ an hour to 1 hour (varying, of course, with the quantities taken) the apparatus is allowed to cool, the receiver removed and closed with a stopper of the same metal, or with a cork wrapped in lead foil.

If the acid be not required in so concentrated a

state, 3 parts of water are first put in the receiver; the mouth of the tube, however, must not dip in the water, or, on the slightest cooling of the apparatus, absorption in the evolution-bottle would ensue.

Recapitulation.—Fluor spar is fluoride of calcium (CaF), which is decomposed by concentrated sulphuric acid, in the presence of water, hydrofluoric acid being given off and sulphate of lime formed.

1 at. CaF, and 1 at. $SO_3 + HO$, form
1 at. $CaO + SO_3$, and 1 at. HF.

586 Parts of fluor spar require 613 parts of hydrated sulphuric acid, but in order to assist its decomposition it must be made into a thin paste; hence the quantity of sulphuric acid is more than doubled. At the gentle heat which is necessary to evolve the hydrofluoric acid no sulphuric acid can pass over.

Properties.—Concentrated hydrofluoric acid is a colourless, very volatile liquid, of a most penetrating smell, and excessively corrosive action on the animal economy. Its most excellent property, either concentrated or dilute, is the power it possesses of acting on glass, (corroding it). The corrosion is caused by the formation of fluoride of silicon, silico fluoride of the metal, hydrofluosilicic acid and water. In order to understand this process, treat a glass consisting of 3 at. potash and 6 silicic acid, $= 3KO + 6SiO_3$ with hydrofluoric acid.

6 at. SiO_3, and 18 at. HF, form
6 at. SiF_3, and 18 at. HO; further,
6 at. SiF_3, and 6 at. HO, form
2 at. $(2SiF_3 + 3HF)$, and 2 at. SiO_3; finally,
3 at. KO, and 1 at. $2SiF_3 + 3HF$, form
1 at. $3KF + 2SiF_3$, and 3 at. HO.

Thus the final result of the action is silico fluoride of potassium $(3KF + 2SiF_3)$, hydrofluosilicic acid $(2SiF_3 + 3HF)$, silicic acid $(2SiO_3)$, and water

(15HO), which, assembled in one formula, is that—

3 at. KO, 6 at. SiO_3, and 18 at. HF, form
1 at. $3KF + 2SiF_3$, 1 at. $2SiF_3 + 3HF$, 2 at. SiO_3, and 15 at. HO.

The ordinary glass, besides silicate of potash or soda, contains silicate of lime, which causes the formation of silico fluoride of calcium; in order to render the formula as simple as possible, I have omitted the lime. The corroded glass has a dull appearance after the action of the fluoric acid vapours on it, owing to the (difficultly-soluble) fluosilicate of potash, and the insoluble free silicic acid remaining fixed on the roughened surface. When liquid fluoric acid is employed, these two substances are dissolved and washed away, the corroded glass appearing clear like the uncorroded. If the fluor spar employed contain silica, the acid will be contaminated with fluosilicic acid, for when the fluoride of silicon formed comes into contact with water, the following ensues :—

9 at. HF, and 3 at. SiO_3, form
3 at. SiF_3, and 9 at. HO ; further
3 at. SiF_3, and 3HO, form
1 at. $2SiF_3 + 3HF$, and 1 at. SiO_3.

In order to detect the hydrofluosilicic acid, either add a solution of a baryta salt, which, being precipitated as fluosilicate of baryta, causes a cloudiness :—

1 at. $2SiF_3 + 3HF$, and 3BaCl, form
1 at. $3BaF + 2SiF_3$, and 3 at. HCl ;

or, some of the acid is evaporated to dryness in a platinum crucible, when the fluosilicic acid is decomposed, and silica remains behind :—

1 at. $2SiF_3 + 3HF$, and 6HO, form
2 at. SiO_3, and 9 at. HF.

ACIDUM HYDRIODICUM.

Hydriodic Acid.

FORMULA: HI + xHO.

Preparation.—A sufficient quantity of iodine is rubbed with six times its weight of pure water, placed in a high narrow cylindrical glass vessel, and sulphuretted hydrogen passed through the mixture (which is kept well stirred with a glass rod), until the lumps of sulphur which form, and must frequently be taken out and broken up, no longer show any brown colour in their interior; (free iodine). As a source of sulphuretted hydrogen it is best to use sulphuret of iron, 4 parts of which are necessary for 3 parts of iodine. The decomposition of the sulphuret of iron will be described under the article "ACIDUM HYDROSULPHUR." The liquid, being milky from containing sulphur, is now filtered, heated to boiling some minutes in a porcelain dish, to dissipate the excess of sulphuretted hydrogen, again filtered if necessary, and immediately poured into a stoppered bottle.

Recapitulation.—When the iodine in solution comes in contact with the sulphuretted hydrogen (HS), the hydrogen of the latter combines with the iodine, forming the readily-soluble hydriodic acid, whilst the sulphur precipitates in pale yellow flocks. At first the reaction goes on slowly, as the iodine is only slightly soluble in water; so soon, however, as some hydriodic acid has been formed, the process quickens, the acid having a far greater solvent power over the iodine, and consequently a more rapid decomposition of the sulphuretted hydrogen ensues. 1 At. iodine requires 1 at. sulphuretted hydrogen.

1 at. I, and 1 at. HS, form
1 at. HI and S.

1 At. HS is formed from 1 at. of sulphuret of iron (FeS). For 1586 parts of iodine 550 parts of sulphuret of iron will, according to theory, be sufficient; experience teaches us, however, that at least 2000 parts of the latter are necessary, a large portion of the sulphuretted hydrogen escaping undecomposed. To lessen this considerable loss as much as possible, the formation of hydriodic acid may be combined with some other process, in which sulphuretted hydrogen can be used,—as, for instance, the precipitation of some metals. For this purpose, the glass in which the iodine and water are contained must be connected, by means of a tube, with a Wolf's bottle, having three perforations; one of these serves to admit the tube through which the gas is passed, another as an exit tube, and the centre one, through which the mixture may be stirred, must be corked up. One disadvantage always accompanies this saving, viz. the difficulty of getting out or thoroughly breaking up the lumps of sulphur.

Properties.—Hydriodic acid is a colourless liquid, of a sour taste and penetrating sour smell, entirely volatile by heat. In well-closed and filled vessels it is unchanged; should the vessel not be quite full, or frequently opened so as to admit the air, the acid at first becomes yellow, and gradually darkens. The oxygen of the air abstracts the hydrogen from the acid and forms water, the liberated iodine remaining dissolved in the hydriodic acid.

1 at. HI, and 1 at. O, change to
1 at. HO and I,

which causes the formation of the so-called hydriodous acid, $HI + I = HI_2$. If the sulphuretted hydrogen employed be not previously washed the acid may contain *iron* and *sulphuric acid*. The first remains behind on evaporation, and is also de-

tected by the black precipitate (sulphuret of iron), on supersaturating the hydriodic acid with ammonia, and adding sulphide of ammonium. The sulphuric acid is detected by the white cloudiness caused on adding a drop of solution of nitrate of baryta.

ACIDUM HYDROTHIONICUM.

Acidum Hydrosulphuricum.—Aqua Hydrosulphurata. Sulphuretted Hydrogen Water.—Sulphide of Hydrogen.

FORMULA: $HS + xHO$.

Preparation.—7 Parts of dilute sulphuric acid (1 part of concentrated mixed with 5 parts of water) are put in a flat-bottomed flask, which would hold as much again; to this is fitted the shortest stem of a double-limbed glass tube, by means of a good cork, the longer stem being also passed through a cork to the bottom of a Wolf's bottle containing a few ounces of water. The other neck of the Wolf's bottle is connected with the shorter end of a similar tube, the longer limb of which is passed to the bottom of a bottle containing 32 parts of distilled water. The accompanying woodcut will render this explanation more clear,—

(*a*) is the gas-evolving bottle, (*b*) the wash bottle, (*c*) the bottle filled with distilled water. When

everything is arranged, the cork of the bottle (*a*) is raised, 1 part of sulphuret of iron added to the acid, and the bottle again quickly closed; the evolution of the gas, which soon commences in the cold, is hastened by a gentle heat, for which a sand bath is most convenient. The mouth of the bottle (*c*) is kept lightly closed during the operation by means of a strip of bladder. As soon as no more gas bubbles are evolved, the corks (*d*) and (*e*) are removed, and the contents of the bottle (*c*) immediately poured into 4 and 8 ounce bottles (previously fitted with corks); the full bottles are corked and sealed over, then placed in an inverted position in a dark cool place.

Instead of pure dilute sulphuric acid, the residue of the ether manufacture, reduced to a spec. grav. 1·125 with water, may be used.

Recapitulation.—Sulphuret of iron consists of 1 at. iron and 1 sulphur = FeS. Brought in contact with dilute sulphuric acid, water is decomposed, the oxygen converts the iron into protoxide, which combines with the sulphuric acid; the hydrogen of the water, with the liberated sulphur, forming a gas, (sulphuretted hydrogen,) which is evolved. 1 At. sulphuret of iron requires 1 at. sulphuric acid, and 1 at. of water:—

1 at. FeS and 1 at $SO_3 + HO$, form
1 at. $FeO + SO_3$ and 1 at. HS.

(The excess of water in the dilute acid is of use in promoting the action, by keeping in solution the salt which forms.)

For 550 sulphuret of iron 613 parts of monohydrated sulphuric acid, or 3678 parts of dilute acid, are sufficient; in the proportions given, that the acid is in a very slight excess, is of no disadvantage. The bottle (*b*) is necessary to free the gas from any iron or sulphuric acid, that may be carried over in a mechanical state, by passing it through water.

It remains to be shown whether the 32 parts of water are entirely saturated by the gas evolved from 1 at. of sulphuret of iron. 1 Part sulphuret of iron yields by weight 0·38 parts of gas of a spec. grav. 1·19 (air = spec. grav. 1·0,) or which is 650 times lighter than water. 1 Vol. of water absorbs, at an ordinary temperature, 3 vol. of gas, or 32 vol. of water, absorb 96 vol. of gas. These 96 vol. of gas weigh 0·147 parts, so—650 : 1 : : 96 : X = 0·147.

Out of the 0·38 parts of gas formed from 1 part of sulphuret of iron, 0·233 parts (or 152 vol.) are lost; this, however, cannot be avoided, as experience shows that in every bubble a part only becomes absorbed.

A small quantity of sulphuretted hydrogen is lost also in another way: during the process the surface of the liquid in the evolution bottle is covered, in patches, with a small coating of sulphur, which arises from the action of a portion of the hot uncombined sulphuric acid, in the form of vapour, on the sulphuretted hydrogen:—

$$HS \text{ and } SO_3, \text{ form}$$
$$S, SO_2 \text{ and } HO.$$

The sulphurous acid thus formed, is however immediately decomposed with another portion of sulphuretted hydrogen into sulphur and water:—

$$SO_2 \text{ and } 2HS, \text{ form}$$
$$3 \text{ at. S and 2 at. HO},$$

occasioning a fresh precipitation of sulphur.

The residue in the flask (*a*) is taken out, and, if in any quantity, may be used for sulphate of iron, oxide of iron, and so on.

Properties.—Sulphuretted hydrogen water is colourless, with a disagreeable odour of rotten eggs, and of a slightly acid reaction. In bottles not quite full, or imperfectly corked, it becomes milky, a white powder is thrown down, and this can go on until

the water contains no scent of the gas. The oxygen of the air, in this case, abstracts the hydrogen, forming water, and the sulphur is precipitated:—

1 at. HS and 1 at. O, form
1 at. HO and S.

This sulphur always contains a little sulphuretted hydrogen, chemically combined, consequently it does not possess the yellow colour of ordinary sulphur, but resembles, in this respect, milk of sulphur. If the washing of the gas is omitted it may contain sulphuric acid, and then causes a turbidness with chloride of barium.

Remarks.—In order to preserve the gas, in a bottle that has been opened, as long as possible, it should, after being well corked, be inverted in a vessel of cold water entirely to cover the neck.

ACIDUM LACTICUM.

Lactic Acid.

FORMULA: $C_6H_5O_5 + HO + \bar{L} + HO$.

Preparation.—100 Parts of sour whey (if this is not to be obtained, take skim-milk, and expose it at a medium temperature (from 60°—70° Fah.) in open glass vessels, until entirely coagulated, then strain,) are placed in a basin capable of holding ½ more, and 5 parts of powdered sugar of milk dissolved in it; 12 parts of crystallized carbonate of soda, rubbed very fine, are put in a well-closed bottle; then, with small portions of it at a time, neutralize the free acid of the milk. The basin is then placed where the temperature is never below 59° Fah., or exceeds 77° Fah., and every one or two days the free acid is saturated with the soda; this is to be repeated until the liquid, after standing four or

five days, gives no longer an acid reaction. This point will be reached when 11 parts of soda have been used. If during its exposure (probably 14 to 21 days) so much evaporation has taken place, that only 40 or 50 parts of whey remain, the glass will, in all probability, when cold, and after standing some days, contain a quantity of lactate of soda in good-sized transparent oblique rectangular prisms. The turbid fluid is now faintly acidified with a few drops of dilute sulphuric acid, the white of an egg added, and the whole boiled, strained through linen and evaporated—first on the sand bath, but afterwards on a water bath—with constant stirring until it attain the consistence of a soft extract, then digested with alcohol of 90 per ct. To the alcoholic mixture, not separated from the undissolved portion, is added concentrated sulphuric acid, equalling $\frac{1}{3}$ by weight of the carbonate of soda employed. After well shaking, and then resting several hours, it is thrown on a linen strainer, the residue washed several times with alcohol, and the clear liquid mixed and filtered. In order to obtain the spirit from this still impure solution of lactic acid, about 20 parts of water are added and placed in a retort, with carbonate of lime $\frac{1}{3}$ in weight of the carbonate of soda employed, then distilled until about 20 parts of fluid remain. The aqueous residual solution of lactate of lime is poured into a porcelain dish and gently warmed as long as it smells of alcohol, filtered whilst hot, and allowed to stand some days in a cool place.

The warty groups of crystals which separate after a time are removed from the mother liquor, the latter evaporated, and again allowed to crystallize; this is repeated so long as any salt separates. The mother liquor, after the second crystallization, is generally very dark coloured, and must, previous to evaporation, be treated with freshly-heated wood charcoal. The whole of the salt will equal, when

dried at a gentle temperature, rather more than 5 parts the weight of sugar of milk employed. Should it not be quite white, the crystallization must be repeated. In order to obtain the pure lactic acid, precipitate the watery solution with oxalic acid, taking the precaution to add no excess, (5 parts of crystallized lactate of lime require 2·06 parts of crystallized oxalic acid,) filter from oxalate of lime, and evaporate the solution in a water bath until no further loss of weight occurs. An air-pump is preferable to remove the last trace of water, as when heated in the air for some time, the concentrated acid acquires a yellow tint. In order to abstract the water, a dish of anhydrous chloride of calcium is placed on the plate of the air-pump, near the lactic acid, and renewed as often as it becomes liquid. 100 Parts of whey yield, when treated as above, about 3 parts of concentrated lactic acid.

The process will certainly be simplified if the lactic acid is saturated with carbonate of lime, 4 parts to 5 of milk sugar, instead of with soda, and then at once treated with sulphuric acid; still it appears to me that nothing is gained thereby, as the acid acts on and is saturated with it but slowly; this might be obviated by raising the temperature, but then a great quantity of the lactic will be converted into butyric acid. The acid is, of course, more readily saturated by caustic lime than by carbonate, but a sufficient quantity for its entire neutralization must not be used, as the action of the lime on the caseine causes such a filthy odour, resembling rotten flesh, that even after the acid has again been separated, will be somewhat insupportable.

Recapitulation.—Cow's milk consists of an aqueous solution of milk-sugar, and caseine, in which a certain quantity of fat (butter), in shape resembling little globules, owing to a quantity of hardened insoluble caseine which surrounds each globule and

causes it to be suspended, forming an emulsion. Besides this, the milk contains potash, soda, ammonia, lime, magnesia, and iron, combined with hydrochloric, phosphoric, sulphuric, and lactic acids; all these salts, however, with an extractive matter, do not amount to 1 per ct., and, together with the butter, need not, in the manufacture of lactic acid, be taken any notice of. The butter averages about 3, the caseine 4, and the sugar of milk 4½ per ct.; yet, of course, these proportions are very variable. In general the milk has an alkaline reaction; sometimes however, even when quite fresh, it reacts acid. Taken literally, the alkalinity does not arise from a free alkali, but from a combination of caseine with it, in which the base has not quite lost its reaction. The free acid is lactic acid. Exposed to the air, at the ordinary temperature, milk, even when previously alkaline, acquires an acid reaction after a day or two; this is facilitated by gently warming (whilst boiling prevents it), consequently it occurs sooner in summer than winter. On becoming sour, the milk acquires a thickening property, it coagulates. Both appearances are intimately connected. The caseine, which consists of carbon, hydrogen, oxygen, nitrogen, and sulphur, has a great inclination to decompose, and, by so doing, it similarly disposes the milk sugar $C_{12}H_{10}O_{10}$ to decomposition, whereby the latter is gradually transformed into 2 at. lactic acid:—

1 at. $C_{12}H_{10}O_{10}$, forms
2 at. $C_6H_5O_5$.

The acid that is formed unites with the alkali that is in combination with the caseine, in consequence of which the latter is liberated, and, being in a very finely-divided state, and scarcely soluble in water, the whole of the milk is transformed into a thick mass. *The coagulation of the milk then rests on the previous formation of free acid, which, taking up the*

solvent of the caseine (the alkali) causes its precipitation. At the same time, whilst the milk remains quiet, the butter globules rise to the surface, owing to their light specific weight, and form the cream. When the coagulated milk is brought on a strainer, the caseine and cream separate from a tolerably clear, slightly yellow-coloured liquid, the whey; this, besides the salts, contains the undecomposed milk sugar, a portion of dissolved caseine, and a small quantity of fat in suspension. Left to itself, the milk sugar is not converted into lactic acid, but, owing to the action of the dissolved caseine, as previously explained, a vinous fermentation is set up, and, with the assistance of 2 at. of water, carbonic acid and alcohol are formed:—

1 at. $C_{12}H_{10}O_{10}$ and 2. at. HO, form
4 at. CO_2 and 2 at. $C_4H_6O_2$.

On account of its dilution, and the presence of a quantity of nitrogenized organic matter in a state of decomposition, the greater part of the spirit, abstracting oxygen from the air, passes over into acetic acid and water:—

1 at $C_4H_6O_2$ and 4 at. O, form
1 at. $C_4H_3O_3$ and 3 at. HO.

That all the milk sugar, or even the first portion, (which forms lactic acid,) does not undergo the alcoholic fermentation, is accounted for by the necessary, but, at this time, not thoroughly explicable circumstance, that, besides other favourable relations, the vinous fermentation only ensues in the presence of a free acid. So, if we neutralize the lactic acid first formed, with a base (carbonate of soda), before the commencement of the vinous fermentation, a fresh quantity of acid must be produced, and this saturation being repeated as often as necessary (every day or two) the vinous fermentation, (the conversion of sugar of milk into carbonic

acid and alcohol,) though not entirely, is yet, to a great extent, prevented; a large portion of the sugar of milk forming lactic acid, and this lactate of soda. From the circumstance that the whey contains more than sufficient caseine dissolved in it to decompose all its milk sugar, arises the necessity for the addition of a fresh quantity of sugar of milk. The cream (the fat) and caseine of the coagulated milk are separated previous to its saturation with carbonate of soda, as they would only hinder the subsequent purification of the salt.

The liquid, saturated with soda, appears turbid on its gradual evaporation from the separation of finely-divided caseine. In order to separate the latter more readily, the fluid is boiled with white of egg, after being slightly acidified because in an alkaline solution the white of egg is not coagulable, or only partially. The thin clarified solution of salts is then freed from most of its water by evaporation, and treated with alcohol, which takes up the lactate of soda, with a small quantity of extractive matter, and the last (dissolved) portion o. caseine remains behind. From the alcoholic solution the soda is precipitated by sulphuric acid, of which $\frac{1}{3}$ the weight of the soda employed is necessary; the combining proportion of carbonate of soda is about 3 times that of concentrated sulphuric acid. The free lactic acid in the spirit must be combined with lime in order to purify it, and of this $\frac{1}{3}$ of the weight of soda employed is necessary, because the equivalent of the carbonate of lime is about $\frac{1}{3}$ that of the crystallized carbonate of soda. After adding water, the spirit is recovered by distillation. When this has passed over (not before), the acid is saturated with lime in the retort. By crystallization the lactate of lime is obtained in white small warty lumps, which, magnified, appear as thick tufts of fine needles; it has a slightly bitter and scarcely saline taste. It consists of

$CaO + C_6H_5O_5 + 5HO$; its equivalent is 1912. An equivalent of oxalic acid entirely precipitates the lime from its aqueous solution, the free lactic acid not containing a trace of it dissolved. The crystallized oxalic acid ($C_2O_3 + HO + 2Aq.$) has the equivalent 788, consequently 5 parts of lactate of lime require 2·06 parts of oxalic acid entirely to decompose it. Of course the last portion of oxalic acid must be very carefully added in order to avoid an excess, which would render the lactic acid impure.

If we regard the quantity of milk sugar contained in 100 parts of milk as 4, these, with the 5 added to the whey, should, if no other substances were formed, produce 9 parts of lactic acid. But it has been previously shown that it is impossible to prevent a certain portion undergoing the vinous fermentation, splitting up into carbonic acid and alcohol, as, with the formation of a small quantity of acid, all the elements are present. Possibly, or rather, probably, a portion of milk of sugar is converted into other substances, which further investigations are necessary to decide. The quantity of carbonate of soda necessary to saturate it (11 parts), proves that 6 parts of acid are formed, consequently only 6 parts of sugar of milk are transformed into this acid. 6 Atoms of anhydrous lactic acid, = 1021, should moreover yield 12 parts of crystallized lactate of lime ; we obtain, however, owing to unavoidable losses in straining, exhausting, recrystallizing, &c., scarcely the half.

It has also been shown that in the transformation of sugar of milk into lactic acid, too high a temperature must be avoided. For instance, should the temperature reach 86° Fah., or exceed it, a considerable portion of the ready-formed lactic acid is lost, forming, with the addition of the elements of water, *butyric acid* ($C_8H_7O_3$), carbonic acid, and hydrogen :—

2 at. $C_6H_5O_5$ and 1 at. HO form
1 at. $C_8H_7O_3$, 4 at. CO_2, and 4 at. H.

The butyric acid will also be saturated by the alkali, and render the lactate of lime impure; the former acid is easily detected by treating the lime salts with excess of dilute sulphuric acid, when the well-known odour of rancid butter, characteristic of butyric acid, is evolved, especially on warming.

The mother liquor of the lactate of lime, when it no longer yields crystals, is not thrown away, but diluted with water, the lime precipitated with carbonate of soda, the lactate of soda solution filtered from carbonate of lime, evaporated carefully to dryness, and then set aside for making lactate of iron; (*See* that Article.) It is, however, necessary to notice exactly the quantity of carbonate of soda used in precipitating the lime, as on this depends the quantity of sulphate of iron requisite to decompose the lactate of soda in the dry mass.

Properties.—Pure lactic acid is a colourless syrupy liquid, of a strong acid taste, but odourless. Its spec. grav., in this concentrated condition, is 1·215, and contains 9·9 per ct., or 1 at. of water. It forms a clear solution with water and spirit in all proportions; ether dissolves but little. Strongly heated it becomes brown, and evolves penetrating acid fumes, which form a white sublimate, having the composition $C_6H_1O_4$, called metalactic acid. If adulterated with *butyric* or *acetic* acids, these may readily be detected in the cold, or by gently warming.

ACIDUM MECONICUM.

Meconic Acid.—Opianic Acid.

FORMULA: $C_7H_3O_7 + 3HO = Me + 3HO$.

Preparation.—Opium is finely sliced, and digested for 24 hours with four times its weight of distilled water, at a gentle heat, expressed and then treated twice with the same quantity of water. The expressed liquids are allowed to subside, then strained, and caustic ammonia added so long as a precipitate is formed; this is collected on a filter, the yellowish filtrate carefully evaporated to a syrupy consistence in a porcelain dish, mixed with a concentrated solution of chloride of calcium, equalling in quantity $\frac{1}{16}$ of the opium employed, boiled with it, and set aside to cool. After standing some days, the partially-solidified mass is washed with cold water, the residual meconate of lime pressed, dried, and weighed. 1 Part of this is rubbed with 10 parts of water, previously heated to 140° Fah., but not higher, and hydrochloric acid, spec. grav. 1·130, added until the meconate of lime has dissolved (a little sulphate may have formed and render the solution turbid), then filter. On cooling, acid meconate of lime crystallizes; this is collected, dissolved in warm water, and decomposed with half as much hydrochloric acid as the meconate of lime weighed. After standing for half an hour, at a temperature of 140° Fah., it is allowed to cool, and the meconic acid crystallizes out. When, on gently evaporating the mother liquor, &c., all the acid is obtained, it is again dissolved in warm water, which separates still more sulphate, filtered, and set aside to crystallize. The yield is trifling; I obtained $\frac{1}{32}$ of the weight of opium employed.

Recapitulation.—Meconic acid exists in opium in

combination with morphine; in order, when preparing the acid, to save the latter, it is precipitated from the aqueous solution of opium by ammonia, (meconate of ammonia is formed); the process for obtaining the morphine will be hereafter detailed. When the filtered solution of meconate of ammonia, after its concentration, is mixed with chloride of calcium, chloride of ammonium and meconate of lime are formed; the latter crystallizes out, being difficultly soluble. The addition of hydrochloric acid gives rise to the formation of the slightly-soluble acid meconate of lime, and readily-soluble chloride of calcium. The precipitated sulphate of lime does not exist in the opium, but arises from the combination of the sulphuric acid (which, with meconic acid, is present in opium, in combination with the alkaloids,) with the lime salt added to the extract. On the second treatment with hydrochloric acid, the acid meconate of lime is decomposed into chloride of calcium and free meconic acid. It is necessary to guard against the liquid acquiring the temperature of boiling water, as then both the meconic acid and the acid meconate of lime are transformed, with the evolution of carbonic acid, into a new acid, comenic acid, $=C_{12}H_4O_{10}$.

2 at. $C_7H_2O_7$, form
1 at. $C_{12}H_4O_{10}$, and 2 at. CO_2.

Moreover, in order to obtain colourless acid, it is necessary to use pure distilled water, as the common generally contains iron, when red meconate of iron is formed, imparting a reddish or brownish tint to the acid. For the like reason the filtering paper used must first be washed with dilute acid, in order to dissolve out any trace of iron.

Properties.—Pure meconic acid forms colourless, glistening plates, which have generally, however, a red or brownish tint, from containing a trace of

iron. It is odourless, has a sour cooling taste, afterwards bitter, loses its water when warmed, then melts, and, further heated, evaporates, forming carbonic acid, water, and pyromeconic acid, $=C_{10}H_3O_5$.

2 at. $C_7H_2O_7$, form
1 at. $C_{10}H_3O_5$, 4 at. CO_2, and 1 at. HO.

Meconic acid is tolerably soluble in water and spirit. Its chief characteristic is the formation of a blood-red solution on the addition to a persalt of iron; yet even this is shared with some other organic acids, for instance, acetic acid.

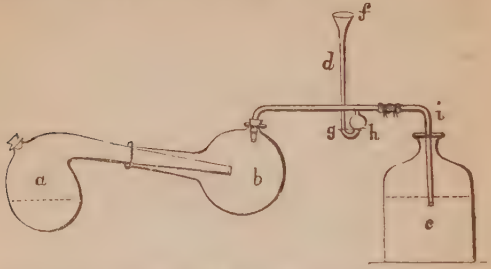
ACIDUM MURIATICUM.

Acidum Hydrochloricum.—Spiritus Salis.—Hydrochloric Acid.—Spirit of Salts.

FORMULA : $HCl + xHO$.

Preparation.—In a tubulated retort, capable of holding twice the quantity of material employed, 8½ ounces of coarsely-powdered common salt are inserted (taking care that none of it lodges in the neck), the retort is placed in a sand bath, and connected with a tubulated receiver by means of a thin strip of warmed caoutchouc, and in the other opening of the receiver is fixed, by a cork, a Welter's tube, bent twice at right angles and closed with quicksilver, the other limb of which is conducted into a bottle containing 8½ parts of distilled water; the tube scarcely requires to dip a line under the water. This bottle must be large enough to hold two or three parts more of water, and is either open or only loosely closed during the process. In order to render the Welter's tube less liable to fracture, it is cut in two, and the pieces connected by means either of a strip or tube of caoutchouc. The above-

mentioned apparatus is best explained by the following wood-cut:—



Through the tubulus of the retort is poured a previously-cooled mixture of 14 parts of concentrated sulphuric acid and 3½ parts of water (the mixture may be made quickly and without danger in a cast-iron or leaden vessel), the opening closed with a well-fitted stopper, and heat applied by means of the sand bath; on this the evolution of gas will directly commence. During the distillation, which proceeds quietly and without danger, the bottle (*c*) must be cooled. When no more gas bubbles are evolved, the fire is removed. The bottle then contains 14 parts of pure colourless acid, spec. grav. 1·145, and the flask (*b*) from 2—2⅛ parts of acid, spec. grav. 1·2; the latter is certainly yellowish, but not otherwise impure. Both may be diluted with the requisite quantity of water.

Recapitulation.—Common salt, when pure, consists of 1 at. sodium and 1 at. chlorine, =NaCl; the commercial, besides this, almost always contains traces of oxide of iron, sulphuric acid, lime, and magnesia, which will not interfere with the process. The chlorides of calcium, magnesia and iron are, however, excessively hygroscopic, consequently common salt is always rather moist.

This moisture, which averages about $\frac{1}{50}$, it is unnecessary to remove, as the acid penetrates the salt much more readily when in a half-moist condition. If the crystals are very large, they may be pounded moderately fine. By the action of sulphuric acid on the chloride of sodium water is decomposed, the hydrogen combines with the chlorine, forming hydrochloric acid, the oxygen with the sodium forms soda, which combines with the sulphuric acid as bisulphate of soda.

1 at. NaCl, and 2 at. $SO_3 + HO$, form
1 at. $(NaO + SO_3) + (SO_3 + HO)$, 1 at. HCl, and 1 at. HO.

733 Parts of chloride of sodium require 1226 parts of hydrated sulphuric acid, which agrees with the above relations ($8\frac{1}{2}$ and 14). The addition of the water serves to prevent too powerful an action taking place. Theoretically speaking, 1 at. of chloride of sodium requires only 1 at. of sulphuric acid to decompose it; in practice, however, it is quite otherwise; and we find, under these circumstances, at least half the salt unacted on, from the soda forming a bisulphate. Now, under two conditions,—which, however, are more important in a scientific than a practical point of view,—1 at. of sulphuric acid will suffice to decompose 1 at. of chloride of sodium:—1st, When the residue is finally heated to redness; or, 2ndly, when the chloride of sodium is entirely dissolved in water; under both circumstances the residue is neutral sulphate of soda. The distilled hydrochloric acid in the flask (*b*) and the bottle (*c*) contains all the chlorine of the salt, when the operation is well performed and the apparatus tightly luted. $8\frac{1}{2}$ Parts of chloride of sodium yield 5·13 chlorine and 5·28 hydrochloric acid. 14 Parts of hydrochloric acid, of 1·145 spec. grav., contain 4·00 parts of chlorine, and 4·11 of anhydrous hydrochloric acid; 2 parts of

hydrochloric acid, spec. grav. 1·20, contain 0·84 chlorine and 0·86 hydrochloric acid; together, 4·84 chlorine and 4·97 hydrochloric acid. The loss of 0·29 chlorine, or 0·31 hydrochloric acid, is chiefly accounted for by the impurity and moisture of the salt employed.

The object of the Welter's tube, instead of the common one, to conduct the gases, is to prevent the absorption of the acid from the bottle (*c*) into the receiver (*b*); for as soon as the apparatus cools, a vacuum being formed in the retort and receiver, the external atmospheric pressure is immediately exerted on the liquid in the open bottle (*c*), and, were the counter pressure wanting, so would the acid from (*c*) be driven up the tube to (*b*); to guard against this, a tube (*d*), bent upwards, furnished below with a bulb, communicates with, and is fused into, the lower part of the horizontal tube (*e*). Above, through the funnel (*f*), some mercury is poured, sufficient to fill the bend from (*g*) to (*h*), consequently during the distillation no gas can escape through the tube (*d*). So soon as the operation is finished, and the vacuum in the retort and receiver begins to form, the acid in the bottle (*c*) is drawn up into the limb (*i*), at the same time the atmosphere, pressing on the mercury in the tube (*d*), drives it into the bulb, and, the air being admitted, the acid in the limb (*i*) again falls; and this continues until the vacuum is filled with air. To render a Welter's tube perfect, the mercury must offer a greater amount of opposition than the acid. This arises from the following consideration:—The height of a column of liquid, counterpoised by the atmospheric pressure, depends on its spec. grav. The spec. grav. of mercury (omitting the fractions) is thirteen times that of water; consequently, a column of mercury 1 inch high affords the same opposition to the atmospheric pressure as a column of water of 13 inches. If we suppose the liquid in

(*c*) to be pure water, of a depth of 13 inches, this will sustain the mercury in the tube (*d*) at a height of 1 inch; but as the water, from absorbing the gas, increases in specific gravity and height, the gas, under these circumstances, will rather drive up and expel the mercury from the tube (*d*) than enter the fluid in (*c*), if the opening of the limb (*i*) dips far below the surface. On this account, the liquid must be scarcely a line in depth above the opening of the tube (*i*); no gas will be lost from this cause, as the water, when saturated, sinks to the bottom, and is replaced by fresh unsaturated.

In the retort, as must now be evident, bisulphate of soda remains. Neutral sulphate of soda (Glauber's salt) is obtained from this by dissolving it in water, and adding milk of lime, until it loses its acid reaction; the sulphate of lime formed is allowed to subside, and the liquor, containing Glauber's salt, evaporated and crystallized.

Properties.—Solution of muriatic acid is a transparent fluid, of a pungent smell and taste, forming, in contact with the air, white fumes (which arise from the watery vapours in the atmosphere increasing in weight, owing to their eager absorption of the gaseous acid), and being entirely volatilized on heating. Its spec. grav. ranges, according to the different pharmacopœias, between 1·11 and 1·14. If the acid has a yellow colour, *organic matter* is the cause (probably from dust). The yellow colour is usually attributed to *iron*, but sufficient of this metal is never present alone to cause it. The iron is detected by supersaturating the acid with ammonia, by which it is precipitated, in brown flocks, as hydrated oxide; the chloride of iron in the solution abstracts the oxygen from 3 atoms of water, and, combined with 3 atoms of water, subsides, whilst the hydrogen of the first 3 at. of water joins the 3 at. of ammonia, and the resulting 3 at. of

ammonium combine with the chlorine of the chloride of iron.

1 at. Fe_2Cl_3, 6 at. HO, and 3 at. NH_3, form
1 at. $Fe_2O_3 + 3HO$, and 3 at. NH_4Cl.

Should the ammonia not cause an instantaneous formation of a floculent brown precipitate, the test glass must be allowed to remain quiet for an hour, the clear liquid decanted from the partially-formed precipitate, and to the latter sulphide of ammonium is added, which causes a blackening (sulphide of iron); or solution of tannin, which changes it to a violet, or bluish black (tannate of iron). If the acid is somewhat reddish, *selenium* is present, which, if the sulphuric acid employed contained it, is almost always the case. The selenium, originally present in the distillate as seleniuretted hydrogen, separates, on standing some time, as a red powder, and may then be readily detected. In the commercial acid there may also be present the following impurities: free *chlorine*, *sulphuric acid*, *sulphurous acid*, *lead*, and *arsenic*. The chlorine, which arises from the distillation of the salt with sulphuric acid containing nitric acid, or nitrogen compounds generally, may be detected by shaking the acid with pure gold leaf, filtering after some hours, and decomposing with a solution of protosulphate of iron, or chloride of tin; the former causes, first, a grayish turbidness, and then a cinnamon-brown precipitate, whilst the latter causes a purple-red colour and turbidness. The free chlorine in the acid dissolves the gold, whilst the protosulphate of iron abstracts the chlorine from the chloride of gold formed, and the gold is precipitated as a brown powder, which by rubbing acquires a metallic lustre.

1 at. Au_2Cl_3, and 6 at. $FeO + SO_3$, form
2 at. Au, 2 at. $Fe_2O_3 + 3SO_3$, and
1 at. Fe_2Cl_3.

Of the result of the action of sesquichloride of tin on chloride of gold, many different views exist; we prefer (as already explained under the article ACIDUM ACETICUM CONC.) that in which oxide of gold, $=AuO$, is combined with an oxide of tin, Sn_2O_3; whilst hydrochloric acid and chloride of tin exist as secondary products.

1 at. Au_2Cl_3, 7 at. Sn_2Cl_3, and 20 at. HO, form
2 at. $AuO + 3Sn_2O_3$ (Purple of Cassius), $2SnCl_2$, and 20HCl.

The sulphuric acid, which arises either by spirting over or else from heating the residue too strongly, is known by giving a white precipitate, with chloride of barium. In order to prevent any mistake, the acid must be previously diluted with three times its volume of water; otherwise, in the *absence of sulphuric acid, a precipitate* may form, owing to the acid abstracting the water from the solution of chloride of barium, which is then precipitated. Sulphurous acid occurs from the same source as the sulphuric, and the presence of a little organic matter in the salt, which abstracts oxygen from the sulphuric acid. In hydrochloric acid having this impurity, sulphuretted hydrogen causes a milkiness, both being decomposed, sulphur and water remaining; (*Vide* ACETIC ACID). The same appearance is also caused if free chlorine be present, nor is it to be depended on should the acid contain arsenic. In order to detect any sulphurous acid with positive certainty, it is better to introduce a piece of pure zinc into the acid, and conduct the gas evolved into a solution of acetate of lead, when a black precipitate will be caused; when zinc comes in contact with hydrochloric acid it abstracts the chlorine, and the liberated hydrogen forms, with

the sulphurous acid, water and sulphuretted hydrogen.

3 at. H, and 1 at. SO_2, form
2 at. HO, and 1 at. HS.

The sulphuretted hydrogen causes a black precipitate of sulphuret of lead in the solution of the lead salt, by giving up its sulphur to the latter, the oxygen of which forms water with the hydrogen of the former. It must, however, be borne in mind, that this reaction is only of value qualitatively, for all the sulphur of the sulphurous acid is not obtained as sulphuretted hydrogen; because, when a portion of this gas comes in contact with the sulphurous acid yet undecomposed, sulphur and water are formed. *Lead* may be present, and arises from the gas being conducted through leaden pipes during the distillation; sulphuretted hydrogen will cause a black precipitate; sulphuric acid, after some time, a white one, and, by evaporating such an acid, chloride of lead will crystallize from it. Finally, *arsenic* is by no means an uncommon impurity, arising from the use of sulphuric acid containing this metal, for the decomposition of the salt. Sulphuretted hydrogen causes, in such acid, a lemon-yellow precipitate of golden orpiment, As_2S_3, readily soluble in alkaline carbonates, whilst the chlorine, previously combined with the arsenic, passes to the hydrogen of the sulphuretted hydrogen.

3 at. HS, and 1 at. As_2Cl_3, form
1 at. As_2S_3, and 3 at. HCl.

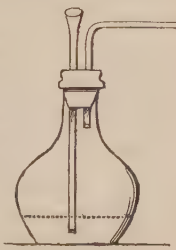
To reduce the sulphuret of arsenic to the metallic state it is rubbed with 4 times its weight of well-dried neutral oxalate of potash ($KO + C_2O_3$), and the mixture heated in a test-tube over the spirit-lamp; just above the substance a metallic ring will be formed, and at the mouth of the tube a smell of

garlic will be evolved. The oxalic acid abstracting oxygen from the potash forms carbonic acid which is evolved, the potassium combines with the sulphur of the sulphuret of arsenic, whilst the arsenic being liberated, volatilizes and is deposited in the cold part of the tube :—

3 at. $KO + C_2O_3$ and 1 at. As_2S_3, form
3 at. KS, 6 at. CO_2, and 2 at. As.

The garlic odour is due to the vapour of metallic arsenic.

A more exact method is that of Marsh, in which the arsenic is instantly obtained in the metallic form; a 4 or 6 ounce bottle is fitted with a well-closed cork, bored with two holes, through one of which is passed the shorter limb of a tube, bent at right angles, the longer limb being drawn out to a fine point at the end, in the second hole is placed a funnel tube reaching almost to the bottom of the bottle. The accompanying wood-cut explains the apparatus. After placing some dried cotton wool in the shorter limb of the tube (to retain any moisture) a few pieces of zinc are put in the bottle, the cork inserted, and so much of the suspected hydrochloric acid poured through the funnel as shall entirely cover the lower end of the funnel tube. The zinc is immediately attacked by the acid, chloride of zinc is formed, and the liberated hydrogen combines with the arsenic, forming arseniuretted hydrogen (As_2H_3) :—



1 at. As_2Cl_3 and 6 at. H. form
1 at. As_2H_3 and 3 at. HCl.

The greater part of the hydrogen is evolved through the open tube uncombined, and mixed with the arseniuretted hydrogen. The arsenic may now be detected as follows: after allowing the gas to escape so long that apparently no more atmospheric air is contained in the apparatus, a light is applied to the opening (*b*), the horizontal limb is heated at the point (*a*), by means of a small spirit-lamp held in the left hand, whilst the right contains a porcelain dish, placed slantwise, but close over the flame at (*b*). Even if the hydrochloric acid contain only a slight trace of arsenic, on the outer portion of the heated part of the tube there will be deposited a metallic ring, and on the porcelain a similar metallic precipitate of arsenic. On holding the nose near the flame (*b*) the smell of garlic is perceptible. By heating as well as combustion the arseniuretted hydrogen is reduced into its elements, but on account of its rapid transition through the heated tube, a portion of the gas will escape decomposition; this, however, is ignited on its exit from the tube, and the metallic arsenic collected on porcelain. Should it give no deposit, more hydrochloric acid must be added through the funnel, as it is possible, if it contain only a small portion of arsenic, that this may have escaped with the hydrogen that was evolved previous to applying the heat. On no account, in order to avoid this loss, must a light be applied to the apparatus when the evolution of the gas first commences, as the atmospheric air then contained in the apparatus forms with the hydrogen a mixture which, on the application of a flame, explodes with fearful violence. The reason of this explosion is the condensation of the two gases to water and the pressure of the external air, which rushes in to supply the vacuum with such force that

even the strongest vessel is shattered, or, more properly speaking, crushed. The loss of arsenic may, however, be entirely prevented by bending the tube (*a*) downwards, and passing the stream of gas through a solution of chloride of soda (hypochlorite of soda.) On entering this solution the aseniuretted hydrogen is decomposed, the hydrogen forming water with the oxygen of the hypochlorous acid; the arsenic combines with oxygen of the soda to form arsenious acid, and the hypochlorite of soda is reduced to chloride of sodium:—

3 at. $NaO + ClO$ and 1 at. As_2H_3, form
3 at. NaCl, 3 at. HO, and 1 at. As_2O_3.

An excess of chloride of soda will, however, convert the arsenious into arsenic acid:—

1 at. As_2O_3 and $2NaO + ClO$, form
1 at. As_2O_5 and 2NaCl.

Consequently in this solution the tests for arsenic acid must be also applied. After the first portions of the gas (excepting the atmospheric air) have been conducted into the chlorinated soda solution, the latter is removed, the lower portion of the glass tube rapidly dried, turned upwards, and the gas treated, as above directed, by heating and combustion. The metallic deposit resulting, in either case, is readily distinguishable from any similarly obtained (antimony for instance) by instantly disappearing on the addition of a concentrated solution of chlorinated soda. Such a solution can still be tested in the moist way, and serve as a corroborative proof.

Purification.—Selenium is entirely deposited on standing some time, and may then be separated from the acid by filtration. Organic matter, lead, sulphuric acid, and iron are left behind on rectification (if sulphuric acid be present it is better to add a few ounces of common salt previously). The dis-

tillation must, however, never be pushed to dryness, and, if iron be present, ½ a pound at least should remain in the retort; the distillate will then contain no trace of iron. Chlorine or sulphurous acid are most readily dissipated by heating the acid in a retort to the boiling point, and, when about ½ has distilled over, changing the receiver. If only chlorine was present, the remainder of the acid comes off pure; but if it also contained sulphurous acid, the rest must be distilled off common salt (that should previously have been added), as sulphuric acid is present. To get rid of the arsenic, digest the acid with $\frac{1}{16}$ of its weight of metallic mercury, in a tubulated retort, with receiver attached, for some days in a sand bath, at a gentle temperature. A little acid is then taken out with a pipette, filtered, if necessary, and sulphuretted hydrogen conducted into it; if it give a yellow precipitate (sulphuret of arsenic) the digestion must be repeated until this is no longer the case; a second digestion is, however, seldom necessary. If sulphuretted hydrogen causes no yellow precipitate, but only a gradual blackening of sulphuret of mercury, the acid in the retort may be filtered, for which doubled printing paper * answers well; or the filtration may be dispensed with, and, after changing the receiver, the distillation of acid proceeded with. The mercury abstracts chlorine from its combination with arsenic, which latter precipitates, as a brown powder, combined with a portion of chlorine, (a sort of sub-chloride). The chlorine that was previously combined with arsenic forms with the mercury a soluble perchloride; consequently the blackening with sulphuretted hydrogen. With a large excess of mercury only insoluble chloride (calomel) should be present, and, by a longer digestion, a portion is formed, but whether

* This is German printing paper, which is far more porous than English.

all the perchloride of mercury first formed precipitates in this manner is doubtful, as we must recollect that here two opposite forces are brought into play—the reduction of the mercury and the solvent action of the hydrochloric acid on the calomel. In order to separate the small quantity of dissolved mercury from the acid, after removing the arsenic, it is subjected to a careful rectification.

The hydrochloric acid, if agitated with mercury, at the ordinary temperature, is entirely freed from arsenic, only a much longer digestion is necessary.

The excess of mercury, after washing and drying, is freed from the adhering powder, by straining through a paper filter, with a very fine hole at the bottom, (a needle puncture). It is now entirely pure, and may be used for any purpose. The loss is inconsiderable.

The mercury may be replaced by copper turnings with the same results, only that a considerable portion is lost, (from dissolving); whilst the remaining copper is with difficulty freed from the adhering arsenic, and serves only for the formation of a salt of copper (sulphate of copper), which is free from arsenic so long as any metallic copper remains undissolved.

ACIDUM NITRICUM.

Spiritus Nitri.—Nitric Acid.—Aqua Fortis.

Formula of the most concentrated :—

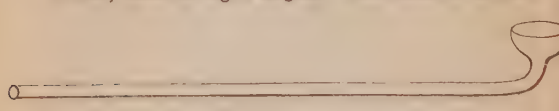
$$NO_5 + HO.$$

Formula of the concentrated :—

$$NO_5 + 5HO.$$

Preparation.—(a) The most concentrated or monohydrate. This, or fuming nitric acid, as it is

called, (although it shares this property with the following, (*b*), is most readily prepared from nitre. 12 Parts of powdered (granulated) nitre are put into a retort, the latter placed in a sand bath, and 12 parts of concentrated sulphuric acid added; it is connected with a capacious well-cooled receiver, and the distillation carried on with, towards the end, a tolerably strong fire, until no more drops appear at the neck of the retort. The end of the process is known by the contents of the retort quietly liquefying. It is not necessary to use a tubulated retort, but, in order to prevent any sulphuric acid touching the neck, it must be poured through a long-necked funnel, bent at right angles. The receiver is not



to be luted, but pushed so far up the neck of the retort that the two are in close contact, because, first, the volatility of the nitric acid is not so great as to cause a great loss; and, secondly, it is impossible to prevent a small portion from forming vapour, which would continually eat through any different portions of luting. The beak of the retort should reach about the centre of the receiver. The distilled product weighs about 7¾ parts.

The nitrate of soda (Chilian Nitre) is not so suitable for the preparation of the monohydrated acid, as the mixture froths up very strongly, and requires, even for the decomposition of a small quantity, a capacious vessel; but with the nitrate of potash the process goes on quietly.

(*b*) *The concentrated, or second hydrate.* For this, the nitrate of soda is the most economical

source. 10½ Parts of commercial nitrate of soda, freed from seeds and other foreign bodies which it contains, are put in a retort, a mixture of 12 parts concentrated sulphuric acid with 3 of water added, and the whole distilled in a sand bath. The decomposition proceeds with a good deal of frothing up. The yield is 11 parts, or a little more than a similar weight of saltpetre.

As in this distillation the strongest acid comes over first, it may, if desired, be kept separate by changing the receiver when about one-third has passed over.

It is scarcely necessary to add, that, according to the state of dilution of the sulphuric acid employed the distillate may be obtained of any strength.

Recapitulation.—Nitrate of potash consists of an atom of potash and one of nitric acid, free from water, $=KO+NO_5$. Like the common salt, and for a similar reason (*vide* HYDROCHLORIC ACID), it requires, even with a sand heat, 2 at. of sulphuric acid for its entire decomposition.

1 at. $KO+NO_5$, and 2 at. SO_3+HO, form
1 at. $(KO+SO_3)+(HO+SO_3)$ and
1 at. NO_5+HO.

1265 Parts of nitrate of potash require 1226 of concentrated English sulphuric acid, which, bearing in mind that the commercial sulphuric acid almost always contains more water than a simple hydrate, agrees with the respective atomic proportions. This excess of water is also a reason why the distillate, which should weigh only 7½, yields at least 7¾ parts. At the commencement of the process, and again at the end, thick brownish-yellow vapours are produced; these are partially given off, but mostly remain absorbed by the acid, which is in consequence discoloured. They proceed from the decomposition of a portion of the nitric acid, and originate in both cases from the same

cause. For instance, at first, when a good deal of sulphuric and but little nitric acid are present, the former possesses the power to abstract a portion of water from the latter, and as nitric acid, after this abstraction of its water of hydration, is not very stable, it is decomposed into yellowish brown vapours of hyponitric acid, $=NO_4$, and oxygen gas. A similar effect to this is caused, at the end of the process, by the bisulphate of potash.

The bisulphate of potash in the retort is either used as such, or, saturated with potash, to form neutral sulphate.

The reason why the nitrate of soda is more difficult of decomposition with the concentrated sulphuric acid than the nitrate of potash, is as follows:—the bisulphate of potash ($KO + SO_3$, $HO + SO_3$) contains no water of crystallization, whilst the bisulphate of soda ($NaO + SO_3$, $HO + SO_3$) is combined with 3 at. water of crystallization. So soon, in the distillation of nitrate of soda with concentrated sulphuric acid, as any bisulphate of soda has formed, it begins abstracting the water from the (hydrated) nitric acid that has been liberated, and from the still uncombined sulphuric acid, by which means a certain degree of dryness is caused in the mass (this, as the action of the sulphuric acid and evolution of nitric acid proceeds with certainty, although slowly, causes the mass to become puffed up), and consequently a continued strong heat is necessary to weaken the attraction of the salt for the water so far that a perfect decomposition of nitrate of soda can take place.

The recapitulation of the process employed for the concentrated acid is exactly similar to the preceding.

1 at. $NaO + NO_5$, and 2 at. $SO_3 + HO$, form 1 at. ($NaO + SO_3$, $HO + SO_3$) and 1 at. $NO_5 + HO$.

1065 Parts of nitrate of soda require 1226 parts of hydrate of sulphuric acid, or $10\frac{1}{2}$ parts of the first to 12 parts of the latter. The extra water that the acid of commerce may contain will be compensated for by the hygroscopic property of the salt. The 3 parts of water used for diluting the acid is about the quantity which the bisulphate of soda requires for its crystallization, viz. 3 at.; consequently, the decomposition will be assisted, and the mixture in the retort kept properly fluid by it; this, as above stated, is the reason why the nitrate of soda is decomposed so much more readily by a weaker acid. The acid therefore, as this additional water finally passes over, is not the monohydrate ($NO_5 + HO$), but, with the hygroscopic water of the nitrate of soda, and the excess over 1 at. of water that the sulphuric acid contains—(*vide* SULPHURIC ACID)—forms the second hydrate ($NO_5 + 5HO$), and weighs 11 parts, in which are contained $7\frac{1}{3}$ parts of the monohydrate. Thus, the advantage of nitrate of soda over the nitrate of potash, consists not only in its being less costly, but also that $10\frac{1}{2}$ parts of the former yields as much acid as 12 of the latter.

The residuary bisulphate of soda may be employed, as described under the article HYDROCHLORIC ACID, in making Glauber's salts.

Properties.—The monohydrated nitric acid forms (on account of the hyponitric acid it contains) a deep golden yellow liquid, of a spec. grav. 1·52, fuming in the air; that made with commercial sulphuric acid is, however, seldom denser than 1·50. The second hydrate (also from the presence of hyponitric acid) is commonly of a yellowish colour, fuming in the air, and having a spec. grav. 1·41. By boiling, the hyponitric acid is dissipated, both acids are then colourless and give off white fumes when exposed to the air; the fumes arise from the great eagerness of the acid to seize more water; so soon as the acid vapours meet with aqueous vapours

in the air, they condense, and combine with them, forming very minute drops; consequently, the fumes are a combination of acid and water in a finely divided state. The colourless acid has a peculiar slight odour, the coloured is sharp and suffocating, both taste intensely acid, readily destroy organic matter, especially animal substances, colouring them yellow, and volatilize completely on heating. Besides hyponitric acid it may contain as impurities chlorine, sulphuric acid, and iodine.

The *hyponitric acid*, as just stated, may be known from the colour it imparts, and the yellow fumes evolved on heating; also by sulphuretted hydrogen water causing a turbidity in it, the hyponitric acid oxidizing the hydrogen of the sulphuretted hydrogen, forming water, and precipitating the sulphur. *Sulphuric acid*, arising either from a portion in the retort spirting over, or some oversight in the manipulation, will, when the acid is diluted with 4 parts of water, give a white precipitate on the addition of a solution of baryta; it is necessary to dilute the acid, otherwise by abstracting water from the solution of nitrate of baryta, it would cause a precipitate of the latter without any sulphuric acid being present. *Chlorine* will be present if the nitre was contaminated with chloride of potassium or sodium; both of these chlorides give off their chlorine as hydrochloric acid by the action of sulphuric acid and the decomposition of water; in contact with nitric acid the hydrogen is abstracted, forming nitrous acid, water, and free chlorine. Nitrate of silver will cause in such nitric acid the casiform precipitate soluble in ammonia. *Iodine*, as iodate of soda, or iodide of sodium, is sometimes present in Chilian nitrate of soda. On distilling from such a nitrate, nitric, iodic and hydriodic acids are given off, the two last by decomposing each other, form water and iodine:—

1 at. IO_5 and 5 at. HI, form
5 at. HO and 6 at I,

a part of which is again converted by the nitric acid into iodic acid, and a portion distils over as iodine. The brown nitric acid containing iodine, will, on standing, gradually lose its colour, the iodine being converted by the action of the acid into iodic acid. This oxydation, however, proceeds so slowly that in such an acid free iodine may almost always be detected; it gives, like chlorine, a precipitate with nitrate of silver, which, in this case, is pale yellow, and insoluble in ammonia. But as such an acid will, in all probability, be contaminated with chlorine, the shortest and most satisfactory method of testing for the iodine, is to dilute it with three times its volume of water, and add some starch paste to the solution, when, after a short time, a more or less blue colour will appear—Iodide of Starch. If there is no reaction with starch, iodine as iodic acid may still be present. To determine this, sulphurous acid is now added, a drop at a time, to the solution, with continuous shaking, and it will then cause the formation of a blue or violet colour if iodic acid be contained. The sulphurous acid reduces the iodic acid to iodine, itself being converted into sulphuric acid :—

1 at. IO_5 and 5 at. SO_2, form
1 at. I and 5 at. SO_3.

The reason why the sulphurous acid must be so carefully added, is because an excess again destroys the blue colour. Commercial nitric acid almost always contains oxide of iron, which is known by the red colour that sulphocyanide of potassium imparts to it when diluted.

Purification.—By boiling the nitric acid, hyponitric acid, free chlorine and iodine are driven off, oxide of iron, sulphuric acid, and iodic acid remain-

ing behind. In order to separate the two last-mentioned acids together with the iron, an ounce or two of pure nitrate of potash is added to the acid previously to boiling; after the hyponitric acid, chlorine, and iodine are driven off, the receiver is changed, and the remainder distilled until a few ounces remain. If, however, it is desirable to lose none of the nitric acid by the distillation, a solution of nitrate of silver is added so long as a turbidity ensues, then some pure nitre and bichromate of potash, and distilled to a few ounces of residue. The iodine and chlorine combine with the silver, the sulphuric and iodic acids to the potash of the nitre, and the second atom of chromic acid in bichromate of potash oxidizes the hyponitric acid to nitric acid; itself, by thus giving off its oxygen, being converted into chromic oxide.

Of course all these newly-formed compounds, together with the iron, remain in the residue. To reobtain the silver employed, it is agitated with a little hydrochloric acid, on account of the excess of nitrate of silver used, the chloride and iodide of silver washed with water, and reduced by heating with carbonate of potash.

Neither nitrate of lead nor nitrate of potash can be used to replace the nitrate of silver for retaining the chlorine or iodine on distilling.

Lastly, it will not be superfluous to mention, that in purifying the nitric acid care must be taken to avoid using a retort which has previously been employed to distil hydrochloric acid, as even by the most careful rinsings, traces of hydrochloric acid will remain in the pores of the glass, and, being driven out by the vapours of the nitric acid, render the latter again impure.

ACIDUM OXALICUM.

Oxalic Acid.

FORMULA: $C_2O_3 + HO + 2Aq$.

Preparation. (*a*) *From binoxalate of potash.*—3 Parts of this salt are warmed, in a capacious porcelain dish, with 12 parts of distilled water, and small portions of carbonate of potash added so long as an effervescence ensues; for this $2\frac{2}{3}$ parts will be necessary. To the still warm liquid sugar of lead is added, with constant stirring, until a small portion, when filtered, gives no precipitate on the addition of a solution of sugar of lead; 9 parts will be generally sufficient. The whole of the contents of the dish is poured into a large stone jar, the latter filled with water, allowed to stand 24 hours; the clear liquid is then drawn off with a syphon, and kept as a solution of acetate of potash; the precipitate is washed with water, until a portion of the clear wash water gives no residue on evaporation; when it is collected on a cloth and dried at a gentle temperature. Its weight is $6\frac{1}{2}$ parts, or somewhat more. 6 Parts of this dry oxalate of lead are gradually added to a mixture of 2 parts of concentrated sulphuric acid and 18 of water, in a porcelain or leaden vessel, gently heated and well stirred for 24 hours, the evaporated water being constantly replaced; the liquid is then decanted, the white salt treated 3 or 4 times with cold water, the precipitate collected on a cloth, and the whole of the liquors mixed and evaporated, in a porcelain or leaden vessel, to crystallization. By evaporating the mother liquors more crystals may be obtained; the last portions form a brown-coloured liquid, which on heating gives off a penetrating sour smell, but yielding no crystals on evaporation, it

may be thrown away. The several lots of crystals may now be dried on blotting paper, with a very gentle heat, dissolved in one-fifth of their weight of hot distilled water, filtered and crystallized. The crystals are again dried on paper. About $1\frac{1}{2}$ parts, or rather more, of oxalic acid is thus obtained from 3 parts of binoxalate of potash. This oxalic acid always contains, even with the most careful manipulation, a small quantity (over 1 per cent) of potash. The quantity of potash may be diminished by rubbing the acid up with 4 parts of cold water, filtering and crystallizing the filtrate. The crystals now yield on calcination a residue scarcely $\frac{1}{200}$ their weight (carbonate of potash). By sublimation of course all the potash remains behind, but in this case a small portion of the acid is always lost by being converted into carbonic acid and carbonic oxide. $C_2O_3 = CO_2 + CO$. When an acid perfectly free from alkali is required, it is best prepared by the following method:—

(*b*) *From Sugar.*—In a retort, which will contain three times the quantity of the materials employed, is placed 1 part of white sugar, in lumps, and 8 parts of nitric acid, spec. grav. 1·4; the retort is placed in a sand bath, and a capacious receiver, containing 1 part of distilled water, connected without luting. The solution of the sugar is now promoted by gently agitating the retort; before the solution is entirely accomplished, a very powerful action ensues (but by no means dangerous, especially if the boiling over of the liquid be avoided), and thick brown yellow vapours pass over into the receiver, which must consequently be well cooled. When the ebullition in the retort has ceased, heat is applied and the acid distilled, leaving about $\frac{1}{8}$; the contents of the retort, still hot, are poured into a porcelain dish, the retort is rinsed with a little water, and the dish placed for 24 hours in a cool spot. The crystalline mass now formed is placed

in a funnel loosely closed with a glass stopper, the crystals washed with a little cold water, and the mother liquor evaporated to half its bulk, to obtain more crystals; these are strained, washed to free from mother liquid, and together with the first quantity dissolved in hot water. The weight of acid will be about half that, or rather more, of the weight of sugar employed.

Recapitulation.—(*a*) The binoxalate of potash consists of 1 at. potash, 2 at. oxalic acid, and 3 at. water, $= KO + C_2O_3$, $HO + C_2O_3$, 2 Aq. By the addition of carbonate of potash ($KO + CO_2$), it is converted into readily-soluble simple (neutral) oxalate of potash, carbonic acid being given off; this is entirely decomposed by sugar of lead ($PbO + \bar{A} + 3$ Aq.); oxalate of lead, $PbO + C_2O_3$, being precipitated as a white insoluble powder, whilst acetate of potash ($KO + A$) remains in solution.

1 at. $KO + C_2O_3$, $HO + C_2O_3 + 2$Aq., and 1 at. $KO + CO_2$, form
2 at. $KO + C_2O_3$;
then,
2 at. $KO + C_2O_3$, and 2 at. $PbO + \bar{A} + 3$ Aq., form
2 at. $PbO + C_2O_3$, and 2 at. $KO + \bar{A}$.

1827 Parts of binoxalate of potash require 865 parts of carbonate of potash, and 4740 parts of acetate of lead; according to this the relative proportions are 3 parts of binoxalate, $2\frac{3}{4}$ carbonate of potash, and 9 parts of sugar of lead, but much more of the two latter are necessary, as the first salt contains a certain quantity of quodroxalate, or a salt containing more acid than the binoxalate, which of course yields a corresponding proportion of acid. For the same reason, the oxalate of lead thus obtained is always nearer seven parts than six, the quantity denoted. However, as the quodroxalate is not always present in the same proportions, the

quantity of carbonate of potash and sugar of lead required will vary. In order to decompose the oxalate of lead an atom of sulphuric acid is requisite.

1 at. $PbO + C_2O_3$, and 1 at. $SO_3 + HO$, form
1 at. $PbO + SO_3$, and 1 at. $C_2O_3 + HO$,

consequently to 1844 parts of oxalate of lead 613 parts of hydrated sulphuric acid are requisite, or 6 parts of the first to two of the latter, which must be diluted with a considerable quantity of water, in order to dissolve the liberated oxalic acid. All the oxalic acid must be again crystallized, in order to deprive it of any small quantity of adhering sulphuric acid.

The acetate of potash, which is obtained as a secondary product, and in a great measure covers the expense of the materials employed, must, for medicinal purposes, be entirely deprived of lead. To effect this, carbonate of potash is added as long as a precipitate occurs, the precipitated carbonate of lead is filtered off, and sulphuretted hydrogen gas passed through the liquors to remove the last trace of lead; allow it to subside, filter, supersaturate in a porcelain dish with acetic acid, and evaporate to dryness. From 3 parts of salt of sorrel about $3\frac{1}{2}$ of acetate of potash are obtained.

The sulphate of lead obtained is also useful as a pigment, but always contains a small quantity of oxalate of lead, which is removed with great difficulty, and renders the yield of oxalic acid rather below the calculated quantity. If an excess of sulphuric acid be employed with a view of preventing this, the oxalic acid becomes contaminated with a trace of sulphuric acid, which is nevertheless entirely removable by a second crystallization.

(*b*) The common white (cane or beetroot) sugar consists of $C_{12}H_{11}O_{11}$; this, brought in contact with

nitric acid, is converted into oxalic acid, by the oxygen of the former (which is reduced thereby to nitric oxide, $=NO_2$), one half of its carbon forming carbonic, the other half oxalic acid, whilst the oxygen and hydrogen of the sugar separate as water.

1 at. $C_{12}H_{11}O_{11}$, and 7 at. NO_5, form
6 at. CO_2, 3 at. C_2O_3, 11 at. HO,
and 7 at. NO_2.

9 At. of the water thus separated go to the oxalic acid, to form the hydrated acid, and the nitric oxide, by absorbing oxygen from the air, is converted into hyponitric acid, $=NO_4$, which is perceptible as a yellow brown vapour. For 2138 parts of sugar 4725 parts of anhydrous nitric acid, or 8750 parts of that having a spec. grav. 1·4 (54 per ct. anhydrous), should suffice; but practice teaches that it is necessary to employ almost twice this quantity, or the yield will be very trifling; and in spite of this, only half as much oxalic acid is obtained as theory denotes; for 3 at. of hydrated oxalic acid, $=C_2O_3+3HO$, weigh 2365, or more than the sugar employed; consequently, half of the sugar is lost in the process. The reason of this loss is the formation of the so-called saccharic acid, $=C_6H_4O_7$, or $C_{12}H_8O_{14}$, ensuing from 1 at. sugar, $C_{12}H_{11}O_{11}$, losing 3 at. of hydrogen and absorbing 3 at. of oxygen. This saccharic acid remains as a very soluble, indeed deliquescent body in the mother liquor; by nitric acid it is converted into oxalic and carbonic acids and water, but it requires treating so many times with nitric acid entirely to effect the decomposition, that it is better to evaporate the mother liquor, and, calculating the residue as sugar, use it as such in the next batch of acid. The yield is, of course, then far greater than from the same weight of sugar.

The contents of the receiver, the vapours com-

bined with water, consist of a tolerably strong nitric acid mixed with hyponitric acid, and may be employed for various purposes.

Properties.—Oxalic acid forms colourless, odourless, oblique rhombic prisms or needles, soluble in 10 parts of cold and 1 part of boiling water, also in alcohol; the solution tastes and reacts strongly acid. Heated, it first loses 2 at. of water of crystallization, and then passes off, mostly undecomposed, as white pungent vapours, without leaving a residue. That prepared from salt of sorrel always contains a little potash, which, on heating, remains behind as carbonate; the acid combined with the potash is decomposed into carbonic acid and carbonic oxide, the latter being evolved:—

1 at. $KO + C_2O_3$, forms
1 at. $KO + CO_2$ and CO.

Any adhering sulphuric acid is detected, on solution, by giving, with nitrate of baryta, a white precipitate of sulphate of baryta, insoluble in nitric acid. Nitric acid is readily detected by the smell, or the solution decolourising a solution of indigo. Commercial acid also contains iron, in which case, after supersaturating with ammonia, hydrosulphuret of ammonia will cause a black and tannin a violet precipitate. No lead need be feared, as combined with oxalic acid this metal is entirely insoluble, even in excess of the acid.

ACIDUM PHOSPHORICUM.

Phosphoric Acid.

Formula of the Fused: $P_2O_5 + HO$.
Formula of the Liquid: $P_2O_5 + xHO$.

Preparation (*a*).—*The fused*; (Acidum Phosphoricum Glacial). 6 Parts of white finely-powdered

bone ash are gradually added to 5 parts of concentrated sulphuric acid and 25 parts of water, in a leaden vessel, and the mixture well stirred with a porcelain spatula; heat is then applied to the vessel, and maintained for a day, the pasty mass being well stirred and the water renewed as it evaporates. As much water as was used to dilute the sulphuric acid is now added, and the mass placed on a strainer, the liquid being returned until it runs through clear; when no more liquid drops, it is mixed with 40 parts of water and strained, this again repeated, the clear liquors mixed and evaporated in the leaden vessel, to about 12 parts. After 24 hours' rest, the liquid in this vessel will contain a quantity of a fine silky crystalline substance, which must be separated through linen, and the liquid, diluted with 24 parts of water, is treated with caustic ammonia so long as a precipitate is formed. 8 Parts of Liq. Ammonia, spec. grav. ·960, will suffice. The white precipitate, after subsiding, is filtered from the ammoniacal liquor, and the latter evaporated, to the consistence of syrup in a leaden, and then to dryness in a porcelain vessel; the greyish-brown salt is exposed in a Hessian, or better in a platinum crucible, to a gradually increased red heat, so long as the smell of ammonia is evolved, the fused mass is then poured out in thin stripes on a sheet of brass, or stone slab (previously warmed). So soon as they are solidified enough, the strips must be taken up and twisted; if this is omitted, they adhere so fast that after completely hardening, it requires a good deal of force to chip them off. When brittle, it is put in a dry bottle and well closed. The yield is about one part.

(*b*) *The liquid;* (Acidum Phosphoricum purum liquidum). 12 Parts nitric acid, spec. grav. 1·20, are placed in a retort, which they must only one-third fill; one part of phosphorus, in whole

sticks, is then introduced, a receiver fitted without luting, and the retort heated over a naked fire, or in a sand bath, until the whole of the phosphorus is acted on. The fire must be very carefully regulated, and slackened so soon as yellow vapours appear in the retort, as through the reaction of the acid on the phosphorus nearly enough heat is generated, and if this become too strong, some of the phosphorus is driven to the surface, and there igniting is very liable to cause the retort to crack. Another evil in heating too strongly is, that much of the phosphorus distils over, unacted on, with the yellow fumes, and in order to avoid this loss, the distillate has again to be poured into the retort. It is scarcely possible to prevent the distillation of some phosphorus, or phosphorous acid; but by proper caution this loss may be reduced to a mere trifle. As soon as no more phosphorus is to be seen in the retort, the contents are allowed to cool, then poured into a porcelain, or, still better, a platinum vessel, heated, and constantly stirred with a platinum or glass rod, so long as any acid fumes are disengaged; the syrupy liquid is then diluted with distilled water, until it weighs ten times as much as the phosphorus employed.

The method usually employed, of gradually adding small pieces of phosphorus to boiling nitric acid, is not only very tedious but entails a great loss of nitric acid and phosphorus.

Recapitulation (*a*).—The bones consist of basic phosphate of lime ($3CaO + P_2O_5$) carbonate of lime and gelatine. By heating in the air, the gelatine is destroyed and there remains a greyish white mass, the so called bone earth equalling 60 or 70 per ct. of the bones employed. This bone earth ordinarily contains about 90 per ct. basic phosphate of lime and 10 per ct. of carbonate of lime (including minute portions of common salt, fluoride of calcium and magnesia). From this the sulphuric acid expels

the carbonic acid, and liberates the phosphoric acid, whilst combining with the lime it forms the slightly soluble sulphate of lime, gypsum. The supernatant liquid, however, is not pure phosphoric acid, but acid phosphate of lime; as even with an excess of sulphuric acid a certain portion of phosphoric acid always remains combined with lime. If we consider the white bone earth, as is ordinarily the case, to consist of 3 at. basic phosphate, and 1 at. of carbonate of lime, we require 10 atoms of sulphuric acid to combine with all the lime present.

3 at. 3 $CaO + P_2O_5$, 1 at. $CaO + CO_2$, and
10 at. $SO_3 + HO$, form
10 at. $CaO, + SO_3$, 3 at. P_2O_5, and 1 at. CO_2.

6475 Parts of bone earth would therefore require 6130 parts of sulphuric acid; but as a certain portion of lime always remains combined with phosphoric acid, so 5 parts of acid are sufficient for 6 parts of bones. The acid solution also contains a portion of sulphate of lime dissolved, which by evaporation and crystallization for the most part separates as a soft glistening silky mass, which may be removed by straining. In order to remove the lime in solution as sulphate as well as that combined with phosphoric acid, the liquid again diluted must be treated with ammonia. By this means the lime is precipitated, not free, however, but as basic phosphate, which causes a considerable loss; the precipitate should therefore be set aside and again treated with sulphuric acid for phosphoric acid. Caustic ammonia is more convenient than carbonate, and precipitates the lime more completely. The precipitate also contains all the magnesia of the bones, as ammonia phosphate of magnesia. The solution which contains phosphate and a little sulphate of ammonia is evaporated to dryness, and heated to redness to drive off the ammonia and sulphuric acid. The salt must not be put into the

crucible all at once as it effervesces considerably. A platinum crucible is the best, it must not however come in contact with the coals, the alkali of which would attack it, but be placed in another crucible (of wrought iron or clay); the space between the two crucibles may be filled up with pure silver sand, chalk, or magnesia. Care must be taken to prevent any pieces of coal from falling into the crucible, which should be well covered with a circular plate of iron, as the carbon would reduce the phosphoric acid to phosphorus, and this combining with the platinum would render it brittle and faulty. A Hessian crucible may be employed; but the acid will then become contaminated with silica, alumina and lime, and this may occur to such an extent that on cooling the acid has a cloudy appearance, from the silica, which then separates. A silver crucible must never be employed, as it is readily attacked by fused phosphoric acid. On account of the precipitate with ammonia being phosphate of lime, the quantity of phosphoric acid obtained is only half that contained in the bones, and which calculation would lead us to expect. The acid liquid should never, as however often happens, be evaporated to dryness and heated to redness without the precipitation by ammonia, for in this case it consists of nothing but acid phosphate of lime.

(*b*) When under the influence of heat nitric acid acts on phosphorus, part of its oxygen converts the latter into phosphoric acid with evolution of nitric oxide, which absorbing the oxygen of the atmospheric air in the retort is converted into hyponitric acid, causing yellow fumes.

6 at. P, and 5 at. NO_5, form
3 at. P_2O_5 and 5 at. NO_2; the latter with
10 at. O = 5 at. NO_4.

The action, however, is not quite so simple, as at first phosphorous acid (P_2O_3) is formed, a portion of

which passes into the receiver with hyponitric and some undecomposed nitric acid. When the contents of the retort, after the solution of the phosphorus, are further evaporated (to a syrupy consistence), the whole of the phosphorus is converted into phosphoric acid by the nitric acid present. This evaporation, consequently so necessary, is best performed in a platinum, but failing this, in a porcelain vessel: the latter however is sure to be attacked by it. The nitric acid distilled off is put aside, and after being brought by the addition of strong acid to a spec. grav. of 1·20, is employed again in the preparation of phosphoric acid.

Properties (*a*).—The fused phosphoric acid forms a brittle transparent colourless glass, very acid, but not corrosive to the taste. In the air it gradually attracts moisture, forming a syrupy liquid. In water or alcohol it should be readily and entirely soluble. If opaque, it contains *silica* and *alumina* (from the crucible), and is not entirely soluble in water. When, although transparent, it is not entirely soluble in alcohol, the presence of *lime* or a trace of *alumina* or *silica* is indicated, the phosphates of which are insoluble in alcohol. To determine whether only lime or the other two impurities are present, it is allowed to subside, the clear solution poured off, and the precipitate treated with caustic potash solution; should it dissolve entirely no lime is present; if however, a portion remain undissolved, lime and possibly silica and alumina are contained; the alkaline solution is filtered, supersaturated with hydrochloric acid, evaporated to dryness in a porcelain dish, and dissolved with the addition of some dilute sulphuric acid in water; if a gritty harsh white powder remains it is silica, and on supersaturating the acid solution with ammonia, a white flocky precipitate indicates alumina. By evaporating the liquid supersaturated with hydrochloric acid to dryness, the silica is changed into the insoluble

condition; but as in this process a portion of the alumina also is rendered insoluble, a little dilute sulphuric acid, which does not affect the silica, is added to dissolve it. Ammonia precipitates the alumina (in this case as phosphate) combining with the sulphuric acid. If sufficient heat has not been employed to drive off the sulphuric acid, nitrate of baryta will cause a precipitate in its solution. For the same reason the phosphoric acid may contain ammonia, which is detected by its peculiar odour on the supersaturation by caustic potash. Traces of ammonia, although not appreciable by the smell, may be detected on holding a glass rod moistened with diluted hydrochloric acid over the phosphoric acid treated with the caustic potash; in this case by the combination of the ammonia with the hydrochloric acid white fumes of sal ammoniac are formed. Any metallic impurities, as *copper*, *iron*, *tin*, *arsenic*, may be detected, the first by ammonia, the second by ferrocyanide of potassium, the third by solution of gold (*vide* Acetic Acid), the fourth by sulphuretted hydrogen (*vide* Hydrochloric Acid). The arsenic, which exists as arsenious acid, and arises from the use of impure sulphuric acid, must be tested for with great care. In order to detect this metal it is not sufficient to add sulphuretted hydrogen water to the phosphoric acid solution, as even if the arsenic is present in a considerable quantity it does not cause an instantaneous yellow precipitate; but a stream of sulphuretted hydrogen gas must be passed through the acid. The yellow turbidity, however, does not always appear instantly. If a black or brown precipitate is caused (copper or tin) it must be quickly filtered, more gas passed through the solution, which is then lightly covered, and set aside for a day. If even after gently warming, it gives no indication of a yellow precipitate of sulphuret of arsenic, but at the most a slight whitish turbidity (from the sulphur of the decomposed

sulphuretted hydrogen) the phosphoric acid is free from arsenic. The absence of arsenic in phosphoric acid can never be determined by means of sulphuretted hydrogen under 24 hours. With Marsh's test the results are more speedy (*vide* HYDROCHLORIC ACID).

(*b*) The acid prepared from phosphorus is an odourless, colourless liquid, of an agreeable but intensely acid taste, and a spec. grav. = 1·160, if ten times the weight of the phosphorus employed. Of this density it contains therefore 10 per ct. phosphorus, or 23 per ct. of phosphoric acid, and 77 per ct. (nearly 25 at.) of water. In testing, besides the impurities enumerated under the glacial, viz. *lime*, *silica*, *alumina*, *sulphuric acid*, and *arsenic*, the following must be searched for: *hydrochloric acid* known by its white curdy precipitate with nitrate of silver; *nitric acid*, if the phosphoric acid not having been evaporated to a syrup contains phosphorous acid, is readily detected by distilling the acid for a little while, when brownish-yellow fumes will be given off, and the contents of the receiver, besides tasting acid, will decolourize indigo solution. The brownish-yellow fumes are due to the action of the nitric acid on the phosphorous acid: should however none of the latter be present, but only nitric acid, this is evolved in white vapours, and is with certainty detected in the distillate. Phosphorous acid, therefore, denotes, either that an insufficiency of nitric acid has been used for oxidizing the phosphorus; or, that it has not been evaporated to a syrup; or, the acid was obtained by burning the phosphorus in the air; it is detected by the fumes of a penetrating garlic odour, which it evolves on evaporation, and by the phosphorescent sparkling so soon as the residue becomes thick. The evolution of light is owing to the decomposition of phosphorous acid, in the presence of water, into phosphoric acid and phosphuretted hydrogen, which latter spontaneously inflames.

4 at. P_2O_3 and 3 at. HO, form
3 at. P_2O_5 and 1 at. P_2H_3.

Another easy method to detect phosphorous acid, is by adding to the phosphoric acid a small portion of red oxide of mercury, and shaking, the red colour is transformed into white and finally into grey. It first forms phosphate of peroxide of mercury, which in the presence of phosphorous acid is again decomposed; the oxide of mercury giving up its oxygen to the phosphorous acid, and separating as a grey powder in the metallic state.

Purification.—The frequent occurrence of arsenic in phosphorus renders it an indispensable duty, before the phosphoric acid is used to test for this poison, and if present abstract it. The best means of testing is by sulphuretted hydrogen gas. If after saturating with the gas and allowing the solution to stand some days, a yellow deposit is formed, this must be filtered; the acid cannot yet be considered pure, but must again be treated with sulphuretted hydrogen, and is only to be looked on as pure when this treatment no longer causes a precipitate of sulphuret of arsenic. To arrive at this point I found it necessary to treat the phosphoric acid four times with sulphuretted hydrogen. The excess of the gas is removed by evaporating the acid to half, the latter is again diluted to its original specific gravity and filtered.

By dissolving phosphorus containing arsenic in nitric acid, the solution after the decomposition has generally a black powder swimming on it, which is metallic arsenic reduced from the arsenious acid by the phosphorous acid.

2 at. As_2O_3, and 3 at. P_2O_3, form
4 at. As and 3 at. P_2O_5.

As all the arsenic is not thus precipitated, filtering off this would not render the treatment with sulphuretted hydrogen unnecessary. The proposed

method of removing the arsenic by heating phosphorus with very dilute nitric acid, is also inapplicable from the fact that phosphorus is far more readily oxidizable than arsenic.

Under the name of acidum phosphoricum depuratum is understood, in some pharmacopœias, an acid obtained by treating the acid phosphate of lime from decomposed bone, with alcohol, which dissolves the free acid, leaving behind the basic phosphate of lime, filtering, distilling off the alcohol, and diluting the residue to a certain specific gravity. The preparation however, will not be perfectly pure; it always contains, without taking into account other impurities, lime and magnesia, and at the present low price of nitric acid and phosphorus is not worth manufacturing.

ACIDUM PHOSPHORICUM ANHYDRICUM.

Anhydrous Phosphoric Acid.

FORMULA: P_2O_5.

Preparation.—In the centre of a porcelain plate, at least 12 inches broad, is placed a small and rather deep porcelain capsule, and in this a piece of phosphorus, not weighing more than two drachms, previously well dried between blotting-paper; this is inflamed and immediately covered with a bell-glass about 12 inches in diameter. The interior space of the bell is immediately filled with thick white clouds, through which are perceived the phosphorescent flame. So soon as this is no longer perceptible the bell is slightly raised in order to admit the external air, and instantly closed again: this is continued so long as any phosphorus remains unconsumed. The covering is then removed, and the light snow-like mass on the bottom of the plate quickly brushed off with a feather, and collected in an air-tight bottle. All that which is not entirely

porous, but has become tough and pasty, remains in the bottom of the plate; and if several portions of phosphorus have to be operated on, the vessels must be rinsed each time with water and carefully dried. The anhydrous phosphoric acid generally weighs about as much as the phosphorus employed.

Recapitulation.—The combustion of the phosphorus results from its combination with the oxygen of the air; it forms chiefly phosphoric acid, that passes off in thick white vapours, which in cooling precipitate as snowy flakes; but on account of the imperfect access of oxygen a part combines with proportionately less oxygen, forming oxide of phosphorus, which covers the inner wall of the little capsule with a red coating. The white flaky mass has a great affinity for moisture, consequently even by the time the process is finished, that portion which lies next the rim of the plate is no longer anhydrous but hydrated phosphoric acid, known by its tough pasty consistence, and as such to be rejected. On account of this twofold loss, viz., hydrated phosphoric acid and oxide of phosphorus, the produce instead of 9 from 4 of phosphorus is only 4 parts.

That which remains adhering to the bell, plate and dish may be rinsed off with a little water, and used as pure phosphoric acid. For this purpose the acid rinse water is mixed with six times as much nitric acid as the weight of burnt phosphorus it contains, and treated as in the preparation of the acid from phosphorus.

If the red oxide of phosphorus is to be saved, the acid rinse waters must be filtered, and the oxide, which the filter retains, washed and dried; it is not however quite pure, but contains small portions of phosphorus mixed with it. In order to remove this, the oxide is spread out in a shallow dish and placed in a moist place, as the cellar. The phosphorus gradually attracting oxygen, forms phosphorous and phosphoric acids: these absorb moisture and cause

the contents of the dish to become a pasty mass. The oxide of phosphorus remains unaltered in this process, and may be freed from the acids by washing.

Properties.—The anhydrous phosphoric acid forms snow-white porous volatile flakes, excessively hygroscopic, which by absorbing water lose their volatility and are converted into a tough mass. A yellow colorization denotes phosphoric oxide. If the phosphorus contained arsenic, arsenious acid must of course be present, and is determined as directed in the preceding article.

ACIDUM STIBICUM.

Antimonic Acid.—Antimonium Diaphoreticum Ablutum of some Pharmacopœias.

FORMULA: $Sb_2O_5 + HO$.

Preparation.—4 Parts of powdered metallic antimony, and 10 parts of nitrate of potash, are intimately mixed with ¼ part of powdered charcoal, and the whole injected by spoonfuls into a red hot Hessian crucible. When the deflagration is finished, the crucible is exposed for half-an-hour to a strong red heat, then allowed to cool, and its contents, at least as much as can be separated from it, powdered, and together with the crucible (to which a great portion adheres tenaciously), boiled with water in a porcelain or leaden vessel, and dilute sulphuric acid added until a decidedly acid reaction is obtained; this requires about 12 parts of dilute acid. The turbid liquor, after separating the crucible, is allowed to subside in a wide earthen pot. After standing four-and-twenty hours, the supernatant liquor is poured off, fresh water added, and this washing repeated as long as the wash liquor

acquires an acid reaction. Lastly, the precipitate is collected on filter paper, or a cloth, and dried with a gentle heat. Its weight will be about 6 parts.

Recapitulation.—In a state of fusion nitre possesses the power of oxidizing substances on which at the ordinary temperature it has no action: this is due to the oxygen of its acid, which is partially given off at a red heat. The nitric acid gives up so much oxygen to the antimony that the latter is converted into antimonic acid = Sb_2O_5, itself being reduced to nitrous acid. The fused mass thus really consists of antimonic acid and nitrite of potash, to which, from the excess of saltpetre employed, may be added nitrate of potash. The process is explained as follows:—

4 at. Sb, and 5 $KO + NO_5$, form
2 at. Sb_2O_5 and 5 $KO + NO_3$; and finally
2 at. $KO + Sb_2O_5$, 3 at. $KO + NO_3$ and 2 at. NO_3.

To 3224 parts of antimony, therefore, 6325, or almost double its weight of saltpetre, are required. The excess of saltpetre in the relation of 4 to 10, is partly to make sure that all the antimony is oxidized, and partly to effect the combustion of the charcoal. The only reason for the addition of the charcoal is to assist the oxidation of the antimony, as during its combustion it evolves for the moment a considerable heat, and thus causes the antimony greedily to absorb the oxygen of the nitric acid. Without this, the deflagration of the antimony would go on but slowly. The mixture must not be thrown into the crucible all at once, otherwise the deflagration will cause the greater portion to be forced out again. The continued heating is to insure the entire oxidation of every portion of antimony. By treating the mass with dilute sulphuric acid the antimoniate of potash is decomposed, the potash combining with the sulphuric acid and the

antimonic acid falling as hydrate (combined with 1 at. of water). At the same time, from the action of the sulphuric acid, the nitrate of potash is decomposed, but the freed nitrous acid immediately absorbs oxygen from the air, forming hyponitric acid (NO_4), which is evolved in yellow-brown fumes. On account of this nitrate of potash, the decomposition of which cannot readily be prevented, a larger quantity of sulphuric acid must be used than is necessary to separate the antimonic acid from its base.

The supernatant liquor, which, besides sulphate, contains a little nitrate and nitrite of potash, may be evaporated and crystallized for sulphate of potash.

Properties.—Pure antimonic acid is yellow, but in the hydrated condition, as we obtain it, is a snow white powder. By heating it first loses its water, and becomes yellow, then 1 at. oxygen, and forms the so-called antimonious acid $= Sb_2 O_4$; this, like the hydrate, is white, and really consists of a mixture of oxide of antimony and antimonic acid.

$$2\ Sb_2 O_4 = Sb_2 O_3 + Sb_2 O_5.$$

Antimonic acid has neither taste nor odour, is insoluble in water, and dissolves with difficulty in hydrochloric acid. If the hydrate possesses a yellow or yellowish colour, and retains this after continued heating, that is, after it is converted into the so called antimonious acid, it may contain either *iron* or *lead* from impure antimony. These metals cannot be extracted from the antimonic acid by weak acids, as they are chemically combined with it. Antimoniate of lead is used as a pigment under the name of Naples yellow. In order to determine which of the two or whether both bases are present, the antimonic acid is fused with three times its weight of liver of sulphur, by which it is converted into the very soluble sulphuret of antimony and potas-

sium; the cooled mass is treated with water, and the black residue (sulphuret of iron or lead) well washed and digested with dilute nitric acid. From the nitric acid solution sulphate of soda throws down a white precipitate if lead be present; a red colour with sulphocyanide of potassium indicates iron. If oxide of antimony is present, the antimonic acid yields, by digestion with bitartrate of potash and water, crystals of tartar emetic, after filtering and evaporating.

ACIDUM SUCCINICUM.

Succinic Acid.—Salt of Amber.

FORMULA: $C_4H_2O_3 + HO = \bar{S} + HO$.

Preparation. (*a*)—*The common officinal.* About half fill an untubulated retort with powdered amber, place it in a sand bath, surrounding it as much as possible with sand; attach a capacious receiver, not air tight, and apply a continuous moderate fire, until the amber, which is gradually fused, no longer froths up or gives off white vapours. The receiver must be cooled by a constant stream of cold water. At the end of the process the retort is broken, the crystalline mass in the neck of it is dissolved, then rinsed into the receiver, the contents of which are poured into a narrow cylindrical vessel, and allowed to remain quiet a day or two, until the oily portion has risen to the surface; it is then skimmed off with a little cotton wool, the lower aqueous solution, together with any crystals that may be at the bottom, heated in a porcelain dish, and when all is dissolved, filtered and crystallized. The mother liquor is evaporated so long as anything separates. The crystals are collected on doubled filtering paper, and dried with a gentle heat.

If the residue in the retort is not wanted, the yield of succinic acid may be doubled by previously adding to the powdered amber $\frac{1}{2}$th its weight of concentrated sulphuric acid diluted with a like weight of water, heating in an earthen or iron dish until it becomes of a dark brown, then proceeding as before directed.

(*b*) *Chemically pure.* 6 Parts of common succinic acid are rubbed in a porcelain dish with 36 parts of water, and crystallized carbonate of soda added so long as it causes an effervescence, (for this 15—16 parts suffice), the solution when filtered from the oil which separates, is treated with 3 parts of freshly-heated, coarsely-powdered, wood charcoal, and digested in a glass flask, at a gentle heat for 24 hours; it is then filtered, the clear fluid entirely precipitated with sugar of lead (about 19 parts) allowed to subside, the supernatant liquid, which may be used for acetate of soda, drawn off, the precipitate well washed with water and dried. Its weight will be about 16 parts. It is finely powdered and digested for 2 days with a gentle heat, and constant stirring, in a porcelain or leaden vessel with $\frac{3}{10}$ its weight (that is to say, 16 parts of precipitate with $4\frac{4}{5}$ parts) of concentrated sulphuric acid, previously mixed with twenty parts of water; the liquid filtered off it, the residue well washed with water, and the filtrates evaporated in a porcelain dish to crystallization. The mother liquors yield more acid on evaporation, until finally they contain little else than sulphuric acid. The crystals must undergo one or more recrystallizations to free them from adhering sulphuric acid. The yield will be $4\frac{1}{2}$ parts.

The following method is shorter and even more convenient. 6 Parts of common acid are put in a porcelain dish with 3 parts nitric acid spec. grav. 1·2, and 9 parts of water, and evaporated to dryness under constant stirring with a porcelain or glass rod;

the residue is brought into a glass flask containing 72 parts of water and 3 parts of freshly-heated animal charcoal (purified with hydrochloric acid), and digested several hours in a sand bath: it is filtered whilst hot, the charcoal washed with hot water, and the filtrate evaporated to crystallization. The acid is at once obtained pure by this method, which yields 4½ parts for 6 of common acid.

Recapitulation (*a*).—The succinic acid exists in amber partially free, the remainder being combined with lime, or what amounts to the same thing, as bi-succinate of lime. By dry distillation of the amber the acid is partially sublimed; that which is combined with the lime is decomposed, together with a portion of the resin, by the action of the heat, into several volatile products, as water, acetic acid, empyreumatic oil, carbonic acid, and carburetted hydrogen; to allow the gases to escape, the apparatus must not be put together air-tight, the liquid products remain with the succinic acid in the receiver. An exact formula of this decomposition can scarcely be given, the process being influenced so much by the degree of heat employed, and the time of its continuance; we can only say that the elementary constituents (carbon, hydrogen, and oxygen) become differently grouped. The portion remaining in the retort is the so-called colophony of amber used for varnishes.

By using sulphuric acid this combines with the lime, and liberates the succinic acid, which is almost entirely volatilized without decomposition. But what is gained in a greater yield of acid is lost in another way, as a portion of sulphuric acid (which must be used in excess) in its affinity for water decomposes a portion of the resin, abstracting from it the oxygen and hydrogen, and separating the carbon, thus rendering it useless.

(*b*.) By saturating the common succinic acid with carbonate of soda, the acid of the latter is driven

off with the formation of readily soluble succinate of soda, the greater part of the empyreumatic oil separating. To remove the last traces of this oil, the solution is shaken with freshly-prepared charcoal, which removes all the smell and most of its colour. If, instead of freshly-heated charcoal, the common is used, it will have scarcely any action, its pores being already filled with air and water; the effect of heating is to drive out these, and render the pores susceptible of taking up colouring and odourizing principles. In order to free the acid from soda it must first be combined with lead; by using acetate of lead, insoluble succinate of lead and soluble acetate of soda are formed :—

$$1 \text{ at. } NaO + \bar{S} \text{ and } 1 \text{ at. } PbO + \bar{A}, \text{ form}$$
$$1 \text{ at. } NaO + \bar{A} \text{ and } 1 \text{ at. } PbO + \bar{S}.$$

1 At. = 2019 Succinate of lead requires 1 at. = 613 of hydrated sulphuric acid, or 10 parts—3 parts, for its entire decomposition.

When common succinic acid is heated with nitric acid, the empyreumatic oil is decomposed by the action of a portion of the oxygen of the nitric acid; hyponitric acid is evolved, and odourless but slightly yellow succinic acid remains. To decolourize it, digest with freshly-heated animal charcoal, which must previously have been deprived of all lime by hydrochloric acid, otherwise the preparation will be contaminated with it. Wood charcoal must not be used, as the succinic acid would abstract the potash and lime; with succinate of soda there is no fear of this.

Properties.—The common succinic acid (for medicinal purposes) forms yellowish scales and needle-formed crystals, smelling and tasting of oil of amber; the purified appears as white prisms, odourless, and faintly acid to the taste. They dissolve in 25 parts of cold and 2 parts of hot water, in 3 parts of cold

and 1½ of hot alcohol of 80 per ct.; the solutions have an acid reaction. Heated it melts and volatilizes without decomposition, forming white vapours which excite coughing; the common acid leaves a trace of charcoal, from the empyreumatic oil. An appreciable residue indicates an intentional admixture, and may be of the most opposite kinds: for instance, *tartaric*, *citric*, or *boracic acid*, *sulphate of potash*, *sugar*, *cream of tartar*, &c., or it may be some substance which volatilizes with the succinic acid, as *muriate of ammonia*, or *oxalic acid*. Should the succinic acid evolve ammoniacal fumes on rubbing with caustic potash, and its solution give a curdy precipitate with nitrate of silver, insoluble in nitric acid, muriate of ammonia is present; oxalic acid is known by the white precipitate of oxalate of lime caused in the solution by chloride of calcium; sulphuric or nitric acids which may have volatilized with the succinic acid, are to be detected, the first by its white insoluble precipitate of sulphate of baryta with a baryta salt; the latter from its destroying the blue colour of indigo solution. If the succinic acid leaves a voluminous carbonaceous residue that does not effervesce with an acid, the adulteration may be citric acid, tartaric acid, or sugar. If on saturating a portion of the succinic acid with lime water, a precipitate is formed soluble in muriate of ammonia, the impurity is tartaric acid, which forms tartrate of lime, that is readily soluble in sal ammoniac. If lime water, though giving no precipitate in the cold causes one when heated, it is citric acid, the lime salt of which is more soluble in cold than in hot water. If lime water causes no change, but the aqueous solution has a sweet taste, sugar is present. Effervescence on applying an acid to the residue after burning shows that cream of tartar is present, which by heating forms carbonate of potash. A white residue, soluble in spirit, which then burns with a greenish flame, is boracic

acid; insoluble in alcohol, but soluble in water, and causing a dense white precipitate with a baryta salt insoluble in acids, is sulphate of potash.

ACIDUM SULPHURICUM PURUM.

Pure Rectified Sulphuric Acid.

FORMULA: $2SO_3 + 3HO$.

Preparation.—A convenient quantity, not more than 9 pounds, of concentrated English sulphuric acid (which is only manufactured commercially) is poured into a retort, not tubulated, with a broad short neck, large enough to contain three times the quantity. A thick spiral platinum wire is then introduced together with a $\frac{1}{2}$ per ct. of the acid used, of finely powdered sulphate of ammonia, the retort is placed in a cast iron pot on a thin layer of sand with which it is then surrounded (the retort ought nearly to fill the pot so that the layer of sand is very thin), a cap of sheet iron is placed over it, and the neck dips into a large glass globe (flask) without any luting, a thick platinum wire being laid between the neck of the retort and the receiver to prevent the glass from resting on glass. The apparatus thus arranged is heated, at first gently, and then gradually increased until the bottom of the sand pot becomes slightly red; the receiver must be cooled with a plentiful stream of water. As soon as the acid boils and about one-sixth has passed over, the receiver is changed, the acid now coming over pure. The distillation must be stopped when about $\frac{3}{4}$ of the acid are in the receiver. Suppose everything to have gone on properly, we may calculate on 6 pounds distilling over in 6 hours after the acid begins to boil.

Recapitulation.—Commercial acid always contains impurities which though in many instances of no

importance, yet for special uses require removing; hence the distillation. If no more than $\frac{2}{3}$ are distilled, the residue contains almost all these, with the exception of sulphurous acid either present in the sulphuric acid or formed from its deoxidation when heated, by the carbonaceous matter present, and passing over below the boiling temperature of the acid, is, by changing the receiver at this point, entirely got rid of; before doing this it is better to wait until about one-sixth has distilled off, as this first portion will contain any water that is present; and the pure acid be stronger. If the acid contains nitrogenized compounds, and this is frequently the case, these combined with sulphuric acid pass over with it in the distillation and must be decomposed; for this purpose the addition of sulphate of ammonia is prescribed. This salt when warmed with a great excess of sulphuric acid is decomposed in the presence of nitric oxide or other oxides of nitrogen, into free sulphuric acid, water, and nitrogen gas. With nitric oxide the following takes place:

$$2 \text{ at. } NH_4O + SO_3 \text{ and } 3 \text{ at. } NO_2, \text{ form}$$
$$2 \text{ at. } SO_3, 8 \text{ HO and } 3 \text{ at. N.}$$

Nitric acid gives these results;

$$5 \text{ at. } NH_4O + SO_3 \text{ and } 3 \text{ at. } NO_5, \text{ form}$$
$$5 \text{ at. } SO_3, 20 \text{ at. HO, and } 3 \text{ at. N.}$$

The nitrogen gas is of course given off at the commencement of the operation. The quantity of nitrogenized principles present is always small, and consequently only a minute portion of sulphate of ammonia is requisite. The coil of platinum wire by rapidly conducting the heat from below to the surface, causes the boiling to proceed steadily; without this precaution the ebullition goes on irregularly from a quantity of vapour being suddenly formed, and not only renders it probable that a portion of the contents of the retort will jerk over, but that the

latter will break from the violence. Between the neck of the retort and receiver a platinum wire is placed not only to allow free exit to any uncondensed vapours, but also to prevent the cold neck of the receiver from coming in actual contact with the hot beak of the retort and endangering the fracture of the latter. Nevertheless it frequently happens that during the distillation one piece of glass after another cracks from the beak of the retort and falls into the receiver: this however is not generally sufficient to necessitate the process being stopped (as this occurs most frequently in winter, the summer should if practicable be chosen for the process).

The residual contents of the retort are almost always turbid from the presence of a white flocculent precipitate, not of sulphate of lead, but neutral persulphate of iron; when these impurities are not of consequence, this residue may be employed, as in the preparation of nitric acid, &c. It is not advisable even when the retort is apparently sound to employ it a second time for the same purpose, as it always becomes to a certain extent rotten and almost certain to break.

Properties.—The sulphuric acid obtained as above, is a transparent odourless fluid of an oily consistence, and excessively sour and corrosive. Its spec. grav. if the receiver was changed just as it began to boil or not changed at all, will be lower than that originally taken, and seldom exceeds 1·800, a weak acid passing over first, the stronger coming over afterwards. If it is required of the spec. grav. of the commercial acid 1·844, the receiver must not be changed until about one-sixth has distilled. Of a spec. grav. 1·844 it does not consist, as is usually stated, of equal atoms of anhydrous acid and water, but of 2 at. of acid, and 3 at. of water, and at −29° Fah. it crystallizes; whilst if the receiver is not changed, or only just at the commencement of the boiling,

its contents will mostly crystallize at a few degrees over 32° Fah. In this readily crystallizable condition the acid contains 2 at. of water. If from $\frac{1}{3}$ to $\frac{1}{4}$ is allowed to distil before the receiver is changed the acid will be found to have a spec. grav. of 1·852 and is the simple hydrate $= SO_3 + HO$.

The impurities generally found in sulphuric acid, are *organic matter*, from dust falling into it, known by the brown colour imparted; the reason of this brown, or, with many organic substances, black discolouration, is the separation of carbon owing to the affinity of the sulphuric acid for water and its abstraction of their oxygen and hydrogen in such proportions as form it. If the organic substance does not contain oxygen enough, a portion of the sulphuric acid becomes decomposed into sulphurous acid and oxygen. Generally, however, the sulphurous acid passes off during the distillation (*vide supra*); it is known by its peculiar odour of burning sulphur; and may be yet more accurately determined by the milky turbidity which sulphuretted hydrogen immediately causes in the dilute sulphuric acid, and which is not again taken up by a solution of carbonate of ammonia (*vide* Acid. Acet.) *Arsenious acid* arising from the employment of sulphur containing arsenic is one of the commonest impurities: it is known by the lemon-yellow precipitate of sulphuret of arsenic caused in the dilute sulphuric acid by sulphuretted hydrogen, and readily dissolving in carbonate of ammonia. This reaction occurs with dilute acid containing but small traces only after the gas has been for some time in contact; thus the necessity, if no turbidity is immediately caused, of setting aside for 12—24 hours. The smallest trace of arsenic is detected by means of Marsh's apparatus, (*vide* Hydrochloric Acid). If on diluting the sulphuric acid with water, or still better, with alcohol, a red powder precipitates, it is *selenium*, which, occurring also in sulphur is thus found in

sulphuric acid. Should sulphuretted hydrogen cause a black precipitate or brown discolouration it indicates *oxide of lead*, arising from the use of leaden vessels; the precipitate is more certain if the acid be previously almost neutralized by ammonia. *Oxide of tin*, the leaden chambers being fastened with a solder containing this metal, is present when the sulphuretted hydrogen precipitate digested with hydrosulphate of ammonia and filtered, then evaporated to dryness and heated to redness, leaves a white residue. Hydrosulphate of ammonia dissolves the sulphuret of tin, leaving the sulphuret of lead; by evaporation the solvent of the former is removed and by heating to redness in the air the sulphuret of tin is converted into sulphurous acid that is given off, and non-volatile oxide of tin. *Oxide of iron*, from the materials containing iron, is known by the dilute acid almost neutralized with ammonia, giving a blue precipitate of Prussian blue with ferrocyanide of potassium (*vide* ACETIC ACID); the ammonia added in excess causes a brown flocculent precipitate of hydrated oxide of iron. If on the excess of ammonia being added an almost colourless precipitate occurs, *alumina* may be present; this is determined by shaking the precipitate with solution of caustic potassa, in which alumina is soluble and oxide of iron insoluble, filtering and adding to the filtrate a solution of sal ammoniac, which after a short time causes a turbidity; the potash decomposes the muriate of ammonia, chloride of potassium is formed, ammonia liberated, and the solvent of the alumina being saturated the latter is precipitated. If after the sulphuric acid has been treated with excess of ammonia, oxalate of ammonia should cause a white precipitate, lime is present. To determine the fixed impurities it is, however, better to evaporate about $\frac{1}{2}$ an ounce of acid to dryness in a platinum crucible. Sometimes the previously mentioned compound of sulphuric acid and nitric

oxide formed in the lead chambers remains dissolved in the acid; to detect this, place a crystal of sulphate of iron in the acid, and it will after a short time be surrounded by a brown layer. This brown colour arises from the decomposition of the compound of sulphuric acid and nitric oxide and the absorption of the latter by the salt of iron. If the test is allowed to remain longer or is heated, the colour again disappears owing to the protosalt of iron being converted into a persalt and nitrous oxide passing off.

Additional remarks.—A mixture of 1 part of concentrated sulphuric acid and 5 parts of water forms a dilute acid of a spec. grav. of 1·25.

ACIDUM SULPHUROSUM.

Spiritus Sulphuris.—Spirit of Sulphur.—Sulphurous Acid.

FORMULA: $SO_2 + xHO$.

Preparation.—The same apparatus is employed as for sulphuretted hydrogen. In the flask (*a*) 1 part of freshly heated, coarsely powdered wood charcoal, and 8 parts of concentrated sulphuric acid, in the bottle (*b*) some water to wash the gas, and in the bottle (*c*) 36 parts of distilled water are placed. The flask is best heated in a sand bath, and this continued as long as gas is evolved. On this ceasing, the bottle (*c*), now containing 40 parts, is closed with a glass stopper.

Recapitulation.—In the cold, carbon and sulphuric acid have little action on each other; on heating the mixture, however, the carbon abstracts from the acid 1 at. of oxygen, forming carbonic oxide, which, together with the sulphurous acid formed, is evolved.

1 at. C, and 1 at. SO_3, form
1 at. CO, and 1 at. SO_2.

75 Parts of pure carbon require 613 parts of hydrated sulphuric acid ($SO_3 + HO$), or 1 part to 8. The wood charcoal employed is certainly not pure, but contains several per ct. of mineral substances, together with some hydrogen; against this, however, is to be noted, that commercial sulphuric acid always contains more than 1 at. of water, which, with 1 part of charcoal to 8 of acid, leaves an excess of the former. A little sulphuric acid unavoidably passes over undecomposed, and this is condensed in the wash-bottle (*b*). Only a very small quantity of the carbonic oxide remains to contaminate the sulphurous acid, for, being with difficulty dissolved in water, it nearly all passes into the air. In spite of the excess of carbon, a little carbonic acid is formed, which also escapes with the carbonic oxide.

Properties.—Sulphurous acid, dissolved in water, is a colourless liquid, of the same suffocating smell and taste as is occasioned by burning sulphur. It bleaches litmus paper; if, however, this is immediately treated with ammonia, the blue colour returns; but if allowed to remain long in contact this is not the case,—the colouring matter is destroyed. The acid prepared as above has a spec. grav. of 1·030, containing $\frac{1}{10}$ its weight of anhydrous acid. Its most common impurity, but one of no consequence in many cases, is sulphuric acid; this arises from its absorbing oxygen from the air, and may be detected by the precipitate with baryta salts, insoluble in acids.

ACIDUM SUPERCHLORICUM.

Perchloric Acid.—Oxychloric Acid.

FORMULA: $ClO_7 + xHO$.

Preparation.—To 5 parts of perchlorate of potash add 10 parts of concentrated sulphuric acid and 2 of water, in a retort which must only be $\frac{1}{3}$ full; place it in a sand bath, connect a receiver without luting, and gently warm, keeping the receiver cool. On first heating, the mixture forms a clear liquid, then, with the evolution of white fumes, a thickish saline mass is formed, which continually froths up, and gives out an odour resembling chlorine; at length it again fuses to a clear liquid, and the apparatus is then allowed to cool. The receiver, which will contain nearly $3\frac{1}{2}$ parts, is now placed in a sand bath and warmed for a short time, until all smell of chlorine is lost; the small quantity of hydrochloric acid it contains is precipitated with sulphate of silver, about 10 grains to $3\frac{1}{2}$ oz. of distillate; this, with the sulphuric acid that has distilled over, is thrown down with carbonate of baryta (about 3 drachms to $3\frac{1}{2}$ ounces of distillate); the precipitate filtered and washed. The filtrate, together with the wash-water, is then poured into a previously-cleansed retort, and gently heated (taking care it does not boil) in a sand bath, until the vapours passing off redden litmus paper; then attach a receiver, and distil almost to dryness. When most of the acid has gone over, the residue acquires a yellow colour and smell of chlorine. The distillate is freed from adherent chlorine by gently warming, and preserved in a glass-stoppered bottle. Its weight will be about $2\frac{1}{2}$.

Recapitulation.—When perchlorate of potash is warmed with sulphuric acid, the perchloric acid

separates from the potash and volatilizes, bisulphate of potash remaining.

1 at. $KO + ClO_7$, and 2 at. $SO_3 + HO$, form
1 at. $KO + SO_2$, $HO + SO_3$, and 1 at. $ClO_7 + HO$.

1733 Parts of perchlorate of potash would require only 1226 parts of sulphuric acid, but in order to decompose all the salt, a considerable excess of acid is necessary. From this, however, occurs an unavoidable evil, viz. that the greater quantity (according to my own experiments four-fifths) of the liberated perchloric acid (obviously on account of the high temperature the mass acquires) is decomposed into chlorine and oxygen, which, passing out of the apparatus, prevent the use of luting. A small portion of chlorine together with free sulphuric acid that has passed over are found in the distillate; the former is removed by the silver salt, the latter with carbonate of baryta. Of course these precipitants must not be added in too large quantities. The precipitates must be removed by filtration, otherwise the distillate will be rendered milky from the bumping over which they cause. The distillation answers two purposes,—both to separate any excess of silver or baryta which remain behind, and also to concentrate the acid by removing the wash-water with which it was diluted. Pure water passes over, until the acid has acquired a spec. grav. of 1·224, when the latter begins to distil, at first as a weak acid, but gradually becoming more concentrated, until at length it is only a monohydrate, which is deposited as a thin crust in the cool part of the retort neck; this, however, rapidly absorbs water and dissolves. As the acid becomes concentrated the temperature naturally rises, and causes a portion of the acid to decompose into chlorine and oxygen, so that this

rectified distillate is not obtained quite free from chlorine. When, however, it has been gently warmed, nitrate of silver gives scarcely a trace of hydrochloric acid. To obtain the acid perfectly free from hydrochloric acid, it is advisable to change the receiver when about ⅔ have distilled.

Properties.—Acid prepared as above is a transparent, odourless liquid, of a strong but agreeable acid, and afterwards sweetish taste. It powerfully reddens litmus paper, without bleaching it. Its spec. grav. is 1·224, containing 28 per ct. of anhydrous acid. Of a spec. grav. of 1·120 it contains 19, and 1·180 24 per ct. Neither nitrate of silver nor nitrate of baryta causes any precipitate in it. Heated, it is entirely volatile.

ACIDUM TANNICUM.

Tannin.—Tannic Acid.

FORMULA: $C_{18}H_8O_{12}$.

Preparation.—A convenient quantity of finely-powdered galls is put into a wide-necked bottle, and ether poured on, sufficient to saturate them and leave a layer, about ½ an inch deep, on the surface; (about ⅔ the weight of the galls is necessary). The bottle is well closed, frequently shaken, and allowed to digest 2 days, at the ordinary temperature. A fine linen cloth is then strained over a broad porcelain dish, and the mass poured on it, when a clear greenish-yellow syrup instantly passes through, which consists of a concentrated solution of tannin. To obtain the whole of it, the cloth must be tied up and strongly squeezed in a wooden press; the dry powder is again twice treated with the same quantity of

ether, the porcelain dish containing the three solutions is *very* gently warmed,* and its contents, constantly stirred with a glass rod, thoroughly dried. During the second and third digestion it is well to fold up the straining cloth and put it in the bottle; by this means it retains its flexibility. Gall nuts, even when apparently equally good, vary much in their yield, which I have never found the same from two portions. From 24 parts of galls, my experiments range between 6 and 12 parts.

Recapitulation.—Tannin exists in the gall nut free, the previously-described process is simply dissolving it, and freeing it from its solvent by evaporation. Ether is employed instead of alcohol or water, because it takes up only the pure tannin, leaving the extractive matter of the galls intact. Commercial ether (containing alcohol and water) serves best for this process, as the purer the ether the slighter is its solvent power over the tannin. The ether employed is not collected,† as to reobtain it by distillation is difficult, and injurious to the product. On this ground I do not consider a fourth digestion advisable, as the ether employed would be more valuable than the tannin procurable.

Properties.—Pure tannin, when dried, forms a resinous uncrystalline mass, which rubs to a pale, greenish-yellow, odourless powder, stable in the air, having a strongly astringent taste, and powerfully reddening litmus paper. Water, as well as hydrated alcohol and ether, readily dissolve it; absolute alcohol and ether take up but little of it. As a fluid reagent, it must be kept in spirit, not water,

* The heat may be obtained by placing on a vessel of warm water; there must be no fire or flame of any kind in the room.

† From the high price of ether in England it is better to distil at a very gentle temperature, and risk the decomposition of a small portion of tannin; percolation is also a preferable method of extraction to the one above given.

as with the latter it gradually decomposes, forming other products, (*vide* GALLIC ACID).

ACIDUM TARTARICUM.

Tartaric Acid.

FORMULA: $C_4H_2O_3 + HO = \bar{T} + HO$.

Preparation.—12 Parts of purified tartar are placed in a leaden vessel with 60 parts of water, heated to boiling, and hydrate of lime added by spoonfuls until the acid reaction has disappeared. $2\frac{1}{3}$ Parts of hydrate of lime will suffice. The mixture must be well stirred during the whole time it is heated to prevent any of the salt sticking to the bottom, which would cause the lead to fuse. To the turbid liquor, without continuing the heat, is added a ready prepared solution of 4 parts of fused chloride of calcium in 12 parts of water; the whole of the mixture is poured into an iron pot, or if the quantity be large, into a wooden vat, and allowed to subside for two days. The supernatant clear liquor is drawn off, and the pulverulent residue washed with water until the latter acquires no further taste; the precipitate is then collected on a linen strainer, pressed and dried. Its weight is about 16 parts. 16 Parts of this well-dried residue (tartrate of lime) with a mixture of 6 parts concentrated sulphuric acid and 54 of water, are placed in a leaden vessel and frequently stirred whilst digesting at a moderately warm temperature for 2 days, the water which evaporates being replaced to keep the whole of an equal fluidity. The mass is now collected in a linen bag, strained, pressed and washed until the water has no acid taste. The collected liquids are evaporated in a clean vessel to 24 parts, strained if

necessary, and poured into a porcelain dish; then, with a gentle sand heat, evaporated until a little taken out and cooled mostly solidifies, when the dish is removed to a cool place, and allowed to remain some days. The crystalline mass that separates is drained from the mother liquor, which is again evaporated and the crystals separated; the whole of the crystalline masses are dissolved in twice their weight of pure water, filtered from any lime salt, and again evaporated to the point of crystallization. Should the solution from organic matter, &c., be of a brown colour, a little pure nitric acid is gradually dropped in during the evaporation until the liquid becomes of a pale yellow. The proceeds of this second crystallization must again be crystallized once or twice to free them from any adhering sulphuric acid or lime; the yield will be about 8—9 parts.

Recapitulation.—Purified tartar (without noticing a trifling portion of lime), consists of 1 at. potash, 2 at. tartaric acid and 1 at. water = $KO + \bar{T}$, $HO + \bar{T}$; the hydrate of lime is $CaO + HO$. When these two come in contact, in the presence of water, the second atom of tartaric acid in the tartar transfers itself to the lime and forms an insoluble precipitate, the neutral tartrate of potash remaining in solution. The reaction which is sure but slow in the cold, is much facilitated by the application of heat. To extract the whole of the acid from the neutral potash salt, a lime salt of a more powerful acid must be employed; chloride of calcium answers to this, forming tartrate of lime and readily soluble chloride of potassium.

1 at. $(KO + \bar{T}) + (HO + \bar{T})$, 1 at. $CaO + HO$,
1 at. $CaCl$ and 6 at. HO, form
2 at. $CaO + \bar{T} + 4\ HO$ and 1 at. KCl.

2352 Parts of tartar require according to calcula-

tion 462 parts of hydrate of lime and 693 parts of chloride of calcium, forming 3250 parts of tartrate of lime. On account of impurities in the material, this amount is never however obtained. The decomposition of the tartrate of lime by sulphuric acid is occasioned by the great affinity of lime for the latter;

1 at. $CaO + \overline{T} + 4HO$ and 1 at. $SO_3 + HO$, form
1 at. $CaO + SO_3$ and 1 at. $\overline{T} + HO$.

1625 Parts of tartrate of lime require 613 parts of hydrated sulphuric acid, or 16 parts to 6. The purification of discoloured mother liquor by nitric acid is owing to the latter yielding its oxygen to the colouring matters, forming carbonic acid and hyponitric acid, which are evolved. The nitric acid must be added very cautiously and excess avoided, or a portion of the tartaric acid will become decomposed, and other products, as oxalic acid, be formed and render the product impure. The product from 12 parts of tartar should be 9 parts, but from the several re-crystallizations a portion of the acid is lost in the mother liquors. This loss is less and the quality and purity of the product greater in proportion to the quantity of tartar operated upon.

The chloride of potassium may be saved as a secondary product by evaporation and crystallization; it is however of no great value.

Properties.—Tartaric acid crystallizes in oblique rhombic prisms and pyramids, permanent in the air, odourless, and of a strongly acid but agreeable taste. It is soluble in 2 parts of cold and 1 of hot water, also in alcohol. If it is at all deliquescent it contains either sulphuric acid or lime (bitartrate of lime). *Sulphuric acid* is detected in the aqueous solution by its white insoluble precipitate with chloride of barium; *lime* by oxalate of ammonia; lime is also detected by a turbidity on solution in

alcohol (sulphate or tartrate of lime). Should too much nitric acid have been used, it will decolourize indigo solution, and in this case will probably contain *oxalic acid*, which gives a precipitate with lime water, whilst the solution is still acid. *Metals*, as *tin*, *copper*, *lead*, are detected by solution of gold, *ammonia* and *sulphuric acid* as under ACID ACETIC. As regards lead only the smallest traces of this metal are found in the acid from the use of leaden vessels, and this is removed by crystallization. All other metals must be avoided in the preparation of the acid.

ACIDUM URICUM.

Uric Acid.

FORMULA: $C_{10}H_4N_4O_6$; or, $C_5H_2N_2O_3$.

Preparation.—From Pigeons' excrements.—12 Parts of dried and powdered pigeons' excrements are boiled for one hour with a solution of 1 part of borax in 120 of water in a porcelain or copper vessel, then strained through linen. The turbid brownish liquid is allowed to subside, then decanted, filtered, and saturated with hydrochloric acid; the coloured flocculent precipitate thus caused is collected on a filter, washed, dissolved in solution of caustic potash, and the brown coloured liquid evaporated to crystallization. The last dark mother liquors are thrown away, the salt collected in a funnel, the most coloured portion removed by washing with cold water, then dissolved in hot water, and decomposed with hydrochloric acid. Should it still be yellow it is again dissolved in potash solution and precipitated with hydrochloric acid. The yield of 12 parts of excrement will not be more than $\frac{1}{6}$ of a part.*

* In England, the excrementitious matter from the larger kinds of serpents will be found a more economical source; the treatment with borax is then omitted.

Recapitulation.—Uric acid exists in pigeons' excrements in a free state, and is readily soluble in a dilute solution of borax. Hydrochloric acid precipitates it from this solution by decomposing the borax, the soda of which combines with the hydrochloric acid and the boracic acid remains dissolved. The formation of urate of potash, by dissolving in solution of potash and crystallizing, is to free the acid from the colouring matter with which it is contaminated. From its solution in potash uric acid is thrown down by the more powerful hydrochloric acid.

Properties.—Uric acid separates in white glittering scales, which form a white powder when dry; it is odourless and tasteless, permanent in the air, feebly reddens moistened litmus paper, is almost insoluble in water, requiring 1800 parts of boiling to dissolve it, and is entirely volatilized, with decomposition, on heating. In nitric acid it is soluble on warming, forming numerous products; if the acid be diluted it yields a residue on evaporation, of a red colour; this is due to purpurate of ammonia, and is characteristic of uric acid.

ACIDUM VALERIANICUM.

Valerianic Acid.—Amylic Acid.

FORMULA OF THE SIMPLE HYDRATE:

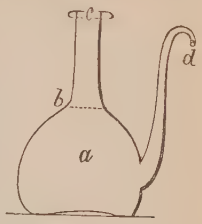
$$C_{10}H_9O_3 + HO = \overline{Va} + HO.$$

FORMULA OF THE TERHYDRATE:

$$C_{10}H_9O_3 + 3HO = \overline{Va} + 3HO.$$

Preparation.—(*a*) *From Valerian root.*—20 Parts of dried and finely cut valerian root are put with 100 parts of water into a copper still, which should not be more than $\frac{3}{4}$ filled, the head luted on, and 30 parts

drawn over. As a receiver, a so called Florentine flask (*a*) answers best, which is previously filled with water to (*b*). From the refrigerator the liquid runs into the neck (*c*), and depositing the oil, which floats on the surface, finally escapes by the opening (*d*), under which is placed a pot to catch the water. The distillate is saturated with powdered crystallized carbonate of soda; to the contents of the retort 30 more parts of water are added,



the same quantity again distilled off, saturated with soda, and the same process repeated as at first. The three neutralized solutions are mixed, evaporated to 4 parts, and filtered into a tarred porcelain dish; then evaporated with constant stirring to dryness, in a sand bath, weighed, and water equal in weight to the salt added to it. The solution is poured into a tubulated retort, and a previously cooled mixture of 1 part of sulphuric acid and 2 parts of water added, (the quantity of concentrated acid used depends of course on the amount of salt; for 5 parts of the latter when dry 4 parts are requisite). The retort attached to a receiver is placed in a sand bath and distilled nearly to dryness. The distillate is poured into a moderately wide cylindrical glass, when the clear supernatant oily layer is removed and kept as a terhydrate of the acid. The solution contained under this may be employed in making valerianates. The quantity of product varies; the maximum I have obtained from 20 pounds of root, was 24 drachms, the minimum 13 drachms, besides the watery solution containing about 8 drachms more. The quantity of ethereal oil obtained as a secondary product was pretty constantly 3 ounces.

To prepare the simple from the terhydrate (which

however is unnecessary for medicinal purposes), the acid is distilled alone, and as soon as it passes over clear the receiver is changed and the remainder preserved as simple hydrate.

(*b*) *From Fuselol.*—Far more advantageous and interesting is the formation of valerianic acid from fuselol, which may be obtained in considerable quantity and at a low cost from the distillers of potato spirit. Before using, it must be thoroughly freed from alcohol and water, with which it is mixed in considerable quantities as it comes from the distillery. This is effected in a tubulated retort, in the tubulus of which is fixed a thermometer graduated as high at least as 370° Fah., the bulb of which must dip in the fluid. It is then boiled until the mercury which at the commencement of the ebullition stood at 212° Fah. reaches 329° Fah. The contents of the retort is now pure fuselol, spec. grav. 0·818. The distillate is alcohol, water, and fuselol, another portion of the latter being obtainable by a second distillation. After these preliminaries the valerianic acid is formed as follows :—

In a tubulated retort, capable of containing twice as much, is placed 5 parts of bichromate of potash, in large pieces, and 4 parts of water : the retort is set in a sand bath, a receiver attached, but not luted, a funnel tube fixed in the tubulus of the retort, so that its lower end dips about ½ an inch in the water, and through it a previously cooled mixture of 1 part of purified fuselol and 4 of concentrated sulphuric acid are poured, in very small portions, at first about 1 drachm, and latterly not exceeding half an ounce. If ½ a pound of fuselol has been mixed with 2 pounds of sulphuric acid, from 2 to 3 hours should be occupied in adding this quantity to the retort. So soon as the reaction which ensues warms the retort so that distillation commences, the receiver is carefully cooled with a stream of water, nor must heat be applied to the retort until the last portions

are added; 4 parts are to be drawn over. When the retort is so far cooled that a drop is some time in collecting at the beak, the receiver is emptied, quickly replaced, a mixture of 4 parts of concentrated sulphuric acid and 6 of water poured, whilst still warm, through the funnel tube into the retort, and the heat continued until 6 parts have come over. Both distillates are saturated with carbonate of soda, of which (for 1 part of fuselol) $1\frac{1}{3}$ of the crystallized is necessary; the saline liquid is evaporated to dryness in a porcelain dish, the salt dissolved in its own weight of water, this solution distilled with sulphuric acid, as described under (*a*). The oily portion on the surface is separated and preserved as terhydrated valerianic acid, and its weight will be somewhat more than half that of the fuselol employed.

Recapitulation.—(*a*) Valerianic acid exists in valerian root, together with an ethereal oil in a free state; both being volatile bodies pass over on distillation with water. In the Florentine flask the ethereal oil, which is but slightly soluble in water, swims on the surface and is separated, the far more soluble acid forming an aqueous solution below. To prevent the root from burning not more than the prescribed quantity must be distilled: the root however being far from exhausted the process is repeated twice again, or until a distillate is obtained having no acid reaction. The contents of the retort even then have an intensely acid reaction, which arises not from valerianic, but from a fixed organic acid. (Malic acid?) This fact shows that even if the valerianic acid were combined with bases in the root, it would be unnecessary to make any special addition of acid (sulphuric acid) in order to set it free. The quantity of soda necessary to saturate the distillate is very uncertain, varying, for 20 pounds of root, from 3 to 6 ounces, the first portion of course requiring most, at least the half of the requisite quantity. By evaporating the saturated liquid

numerous fine particles are formed, doubtless due to the decomposition (oxidation) of the small quantity of ethereal oil in the solution, which must be separated by filtration. In order again to separate the acid in a concentrated form from the soda, the salt, dissolved in an equal weight of water, is decomposed with so much sulphuric acid as will form bisulphate of soda.

1 at. $NaO + \overline{V}a$ and 2 at. $SO_3 + HO$, form
1 at. $(NaO + SO_3) + (HO + SO_3)$ and 1 at. $Va + HO$.

1552 Parts of valerianate of soda require 1226 parts hydrated sulphuric acid, or 5 parts of the first 4 parts of acid. So soon as the acid is added the valerianic acid separates as an oily layer on the surface, distilling with the water, and again separating in the receiver, leaving a concentrated solution of the acid below. It is now generally slightly yellow, but sufficiently pure for the formation of salts. The formation of the monohydrated on distilling the acid alone is owing to water and some acid first passing over, and only when about half finished, that the most concentrated distils. Other substances having a strong affinity for water, as chloride of calcium, are not applicable in this case, as the acid would become contaminated with hydrochloric acid.

The ethereal oil obtained has a slightly acid reaction, which is due to mechanical admixture with a little of the acid, and not from chemical combination with it; a very small particle of soda instantly removes it. If the oil and acid exist in the root in combination, they are separated by water into two unmistakeably different bodies.

(*b*) Purified potato fuselol consists of $C_{10}H_{12}O_2$; but may be considered as a kind of alcohol or hydrate of an ether—$C_{10}H_{12}O_2 = C_{10}H_{11}O + HO$, and its scientific name is amylic alcohol, or hydrated oxide of Amyle. In contact with nascent oxygen it is changed, and converted, when the oxidation is con-

siderable, into water and valerianic acid, also called amylic acid.

1 at. $C_{10}H_{12}O_2$ and 4 at. O, form
1 at. $C_{10}H_9O_3$ and 3 at. HO (that is, the terhydrated acid).

The oxygen necessary for this is derived from the bichromate of potash by the action of sulphuric acid; bisulphate of potash, oxide of chromium and oxygen being formed.

1 at. $KO + 2\ CrO_3$ and 2 at. $SO_3 + HO$, form
1 at. $KO + 2\ SO_3 + HO$, 1 at. Cr_2O_3 and 3 at. O.

1 Atom of bichromate of potash yields only 3 at. of oxygen, and 1 at. fuselol requires 4 at.: hence, according to theory, the quantity of bichromate must be increased one third; in practice, however, even this will be found not nearly sufficient, unquestionably arising from a portion of the oxygen passing off uncombined, whilst another portion serves for other purposes (as the formation of acetic acid, &c.), and also it must be remembered, that under the prescribed conditions (temperature, &c.), chromates are never entirely decomposed by sulphuric acid. The quantity of acid and salt should be trebled, that is, to 1 at. fuselol = 1100, 3 at. bichromate potash = 5574, and 6 at. conc. sulphuric acid = 3678, and the commercial acid always containing more than 1 at. of water, the relative proportions of 1 fuselol, 5 of bichromate and 4 of sulphuric acid will be found the best in practice. But as no sulphuric acid has been allowed for the oxide of chromium formed, the latter combines with a portion of the sulphuric acid, and it is to obtain this that the second quantity of sulphuric acid is added to the contents of the retort. At first sight it appears far simpler to add the whole 8 parts of sulphuric acid at the commencement, but practice has taught me that the product is less in this case, probably owing to

the action being too energetic and a quantity of oxygen escaping, or rather perhaps forming more highly oxidized bodies (as acetic acid).

The addition of the mixture of sulphuric acid and fuselol must be very carefully made and in small quantities, otherwise so powerful a reaction ensues, that without any application of fire, and before the whole of the mixture is in the retort, so much heat is evolved as to cause it to boil. With every precaution there would still be a risk of the contents boiling over, or the retort bursting, if the chromate of potash were powdered instead of being inserted in lumps. On the first distillate is commonly a thin oily layer, which consists of oxidized fuselol, or more properly speaking valerianate of oxide of amyle, $=C_{10}H_{11}O+C_{10}H_9O_3$; on saturating the fluid with soda this is decomposed, the acid combining with the soda, the oxide of amyle being given off on evaporation. It is better, after the first distillation, not to wait to pour the mixture of sulphuric acid and water into the retort until the contents of the latter has entirely cooled, otherwise the mass hardens and closes the funnel tube. If, as we might expect, all the fuselol were converted into valerianic acid, 1100 parts should yield 1162·5 anhydrous, or 1500 parts of the terhydrated acid; the yield with the above process is, however, never more than half the weight of the oil employed. The reason of this immense loss is, that a portion of the fuselol volatilizes either partially or totally unoxidized, and another portion is converted into acetic acid.

2 at. $C_{10}H_{12}O_3$ and 20 at. O, form
5 at. $C_4H_3O_3$ and 9 at. HO.

As acetic acid is soluble in water in any proportion it remains in solution after the distillation of the soda salt with sulphuric acid, the superficial oily layer being pure valerianic acid. Of course this

solution also contains valerianic acid, which, however, is only advantageously applicable to the formation of the difficultly soluble zinc salt, either by saturating with soda and precipitating with sulphate of zinc, or else at once neutralizing with carbonate of zinc recently precipitated. The light saline mass thus obtained is, after carefully expressing, dried at a very moderate temperature.

The contents of the retort, after the distillation, may be used for sulphate of potash and oxide of chromium, and thus reduce the expense. For this purpose, the solid greenish black mass is covered with warm water, in which it very readily dissolves, the whole poured into a narrow necked flask, and sulphurous acid passed into it until it smells strongly of this gas, and a portion warmed with carbonate of potash and filtered yields a colourless solution; it is then transferred to a capacious leaden vessel, diluted with more water, heated to boiling, and solution of potash gradually added until slightly in excess, when after carefully filtering off the oxide of chrome, the solution is evaporated so long as crystals separate. The sulphurous acid gas converts any of the undecomposed chromate of potash into sulphate of potash and oxide of chrome.

1 at. $KO + 2\ CrO_3$ and 3 at. SO_2, form
1 at. $KO + 2SO_3$, 1 at. Cr_2O_3, and 1 at. SO_3.

The sulphuric acid necessary for the solution of the oxide of chromium, and not expressed in the above formula, is already contained in the liquid. By the addition of potash solution, the bisulphate is converted into neutral sulphate of potash and the oxide of chromium precipitated.

Properties.—Pure valerianic acid is a colourless oily-like liquid of a penetrating odour, resembling the volatile oil of valerian, but more disagreeable, approaching that of rotten cheese, and with a sharp loathsome taste, reminding one of valerian.

Both the anhydrous and hydrated float upon water; the spec. grav. of the first is 0·944, and of the last 0·967. The simple hydrate dissolves in 30, the terhydrate in 26 parts of water; the solution has a strongly acid reaction, and together with the properties of the pure acid (in a milder degree), a saccharine taste. Its alkaline salts have a saccharine as well as a valerianic flavour. It is soluble in all proportions of pure alcohol and ether; it is entirely volatilized by heat. Heated in a platinum spoon it readily ignites and burns with a bright flame. Its aqueous solution gives no precipitate with nitrate of silver or nitrate of baryta, otherwise *hydrochloric* or *sulphuric* acid is present. The presence of *acetic acid* is known by diluting the acid with twice its weight of water, saturating with freshly precipitated carbonate of zinc, pressing the precipitate, filtering and evaporating the liquid slowly, when after the separation of some little scales of valerianate of zinc, colourless crystals of acetate of zinc will form.

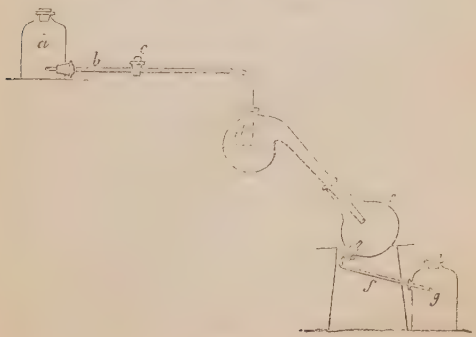
ÆTHER PURUS.

Æther Sulphuricus.—Sulphuric Ether.—Pure Ether.

FORMULA: $C_4H_5O = Ae + O$.

Preparation.—9 Parts by weight of concentrated sulphuric acid (English), and 5 parts of spirit of wine, 90 per ct. (spec. grav. 0·818), are well stirred together by means of a glass rod, in a leaden or cast iron vessel; the latter is then well closed and allowed to cool: in winter this may be facilitated by placing in ice or snow. The acid mixture is then poured into a tubulated retort which must not be more than $\frac{2}{3}$ full: this is placed in a sand bath, surrounded as high as the liquid reaches with sand, and connected by a strip of bladder to a tubulated

receiver, so placed that the tubulus is below, and having a leaden tube bent at right angles luted into it, the other end of which dips into a glass bottle also tubulated at the side. The principal opening of this bottle is well secured by cork and bladder, whilst that at the side through which the leaden pipe passes is simply surrounded with bladder in which is a small puncture to allow the exit of the air in the vessel at the commencement, and avoid any pressure on the surface of the glass vessels. A glass bottle, tubulated near the bottom, is now placed at the distance of several feet from the retort, rather higher than the top of the furnace, having a leaden pipe luted in the lower extremity sufficiently long to reach the retort, into which it dips by being bent at right angles, and having a brass tap in the centre. The tube should be placed so deep in the retort that it is within about one inch of the liquid, the tubulus is then carefully closed with luting and bladder. The top being closed, the bottle is filled with spirit of wine of the previously-named strength. A cut of the apparatus will render its construction more clear.



The heat, as in all distillatory processes, is applied at first slowly, but when the retort is warmed throughout it is considerably increased, and must be sustained at this raised temperature without cessation, the mixture having a far higher boiling point than water, and requiring to be kept in an uninterrupted state of ebullition to insure a good yield. Previously to boiling, a good stream of water is allowed to flow over the receiver (*e*) and not stopped again until the retort is nearly cold. As soon as the contents of the retort boil, the tap (*c*) is slightly turned and spirit of wine allowed to flow into the retort according to the stream through the tube (*f*) into the bottle (*g*), so as always to retain the same height of surface in the boiling mixture. The vessel (*a*) is refilled with spirit as often as necessary; various quantities have been given as requisite; my own experience is, that for 9 parts of sulphuric acid not more than 72 parts be employed, as after this the acid is so weakened that more alcohol than ether passes over. The bottle (*g*) is removed and emptied as often as it is nearly filled to the tubulate. When the last portion of alcohol has passed, the tap is closed and the fire removed; so much, however, distils over from the hot mixture that only a small quantity of spirit remains in the residue. With 9 pounds of acid and 72 pounds of spirit the process may be finished in less than 24 hours. It is better not to discontinue it until finished, or if on account of the necessary light for working through the night any danger is apprehended, the process should be recommenced quite early on the following morning. The greatest care is necessary throughout the distillation, and an absence of more than a quarter of an hour at any time not to be thought of.

15 Pounds, by weight, of the distillate, which has almost always an acid reaction, is shaken with 1 ounce of hydrate of lime and 1 ounce of peroxide of manganese that have previously been well mixed

with water, until it has no further action on litmus paper; it is then rectified in a copper still or by small quantities in glass retorts. What passes over must be occasionally tested with the areometer: so long as the spec. grav. is under 0·750 the distillate is officinal ether; when it exceeds that spec. grav., and its density will gradually increase, it may be used for Liquor Anodynus, the spec. grav. of which will range from 0·825 to 0·830. This is followed by spirit of wine, and when the distillate has only a weak watery taste, the fire is allowed to go out. The yield of ether is not always the same, its mean product is about half the weight of the spirit employed.

It is commonly stated that the raw distillate should be mixed with water until the ether again separates; this is superfluous, as the water then contains a quantity of ether in solution, to re-obtain which another distillation is necessary. The neutralization is affected more readily by using oxide of manganese than simply with lime.

In order to obtain ether free from alcohol and water, the officinal ether is shaken for an hour with its weight of water, and allowed to subside for one hour, the supernatant fluid drawn off with a syphon, rectified with its weight of fused chloride of calcium, and the first portion of the distillate separated from the last, which will contain traces of water.

Recapitulation.—Anhydrous or absolute alcohol consists of $C_4H_6O_2$; in order to explain the process more readily, we will consider it as hydrate of ether $= C_4H_5O + HO$, and the ether as an oxide of a hypothetical radical $C_4H_5 = Ae$. This radical is named Aethyl (from Aether and ὕλη Base) or Ether base, therefore the Ether is Aethyloxide $= C_4H_5 + O$ or AeO; and the alcohol, hydrated oxide of Aethyl, AeO + HO. When alcohol (hydrated oxide of Aethyl) comes in contact with sulphuric

acid, the latter separates from it its water of hydration, which is replaced by 2 at. of hydrated sulphuric acid: these, with the oxide of ethyl, form an acid salt, which is named Sulphovinic acid, or, as we will consider it, bi-sulphate of oxide of Aethyl :—

1 at. $C_4H_6O_2$ and 2 at. $SO_3 + HO$, form
1 at. $(AeO + SO_3) + (HO + SO_3) + HO$, and 1 at. HO.

The atom of basic water may be replaced by a stronger base, as lime or baryta, and sulphovinates are thus obtained, true double salts, having neither an acid nor alkaline reaction, dissolving readily in water, and when dry being anhydrous. Their formula is, therefore, $(AeO + SO_3) + (RO + SO_3)$, in which R, the radical, signifies the second base.

575 Parts of absolute, or 640 parts of alcohol, containing 90 per ct. spirit, would require 1226 parts of hydrated sulphuric acid (or 5 parts of alcohol of 90 per ct., somewhat over 9 parts of hydrated sulphuric acid), entirely to convert it into bisulphate of oxide of Aethyl; but, from some unexplained reason, a small portion of alcohol, and consequently of sulphuric acid, always remains unacted on. When this mixture is heated to 284° Fah.) it begins to boil: the bisulphate of oxide of ethyl is, however, not permanent at this temperature, but, decomposing, forms hydrated sulphuric acid and ether; and the sulphuric acid not being volatile at 284° Fah., remains behind as a hydrate, the ether and some water passing over :—

1 at. $(AeO + SO_3) + (HO + SO_3) + HO$ and
1 at. HO, form
2 at. $SO_3 + HO$ + 1 at. AeO and 1 at. HO.

The formation of the ether then is due to the formation of bisulphate of oxide of ethyl from sulphuric acid and alcohol, and the instability of this body at its boiling point. The hydrated sulphuric acid thus liberated and remaining in the retort, has the property, as before stated, of again combining

with alcohol, with the same results; hence the reason for the addition of alcohol by drops to the boiling mixture. Against the possibility of this new formation of bisulphate of oxide of ethyl may be objected, the temperature of the boiling mixture, which would rather favour a decomposition. To meet this, it may be suggested that the drops of cold alcohol cause a momentary cooling in a small circle, thus allowing the possibility for combination; the next moment, however, the temperature rises, and decomposition again ensues. The chemical process, during the dropping of the alcohol into the boiling mixture, is thus a continuous formation of bisulphate of oxide of ethyl, and its instantaneous decomposition into sulphuric acid, ether, and water.

The above is the real explanation of the formation of ether; it remains now to consider some minor conditions by which the quantity and purity of the product is modified.

By the contact of hydrated sulphuric acid and absolute alcohol, the action of the acid on alcohol must, according to the preceding statement, be endless, and if only ether and water distilled over this would be the case; but, for reasons which at present we cannot control, the process is not entirely so simple; for instance, the sulphuric acid acts as an oxidizing agent on the elements of the alcohol, causing the formation of sulphurous acid, that passes over, and a carbonaceous body remaining behind, which at first is quite soluble, colouring the acid of a deep brown, but gradually increasing (together with sulphurous acid), it separates as a tough black pellicle on the surface. On the composition of this black body there are yet doubts; its elements are carbon, hydrogen, oxygen, and sulphur (C_{80}, $H_{21}O_{20}S_2$?). Another product of decomposition during the process is Oil of Wine $= C_4H_4$, a yellowish thick oil which on rectifying the ether is

commonly found floating on the watery residue. This destructive action occurs with absolute as well as hydrated alcohol, and on account of the high price of the former, alcohol of about 90 per ct. is used. The employment of this alcohol also circumscribes the action of the sulphuric acid, on account of its containing at the outset 10 per ct. of free water. It is clear that in employing this alcohol the acid continually acquires more water, abstracting it from the alcohol, and retaining it with a force which prevents more than a small portion passing over with the ether. There comes, however, a time, when the acid has taken up as much water as, under the circumstances, it can retain (the boiling point of this mixture is only 255° Fah.) Together with the ether, water is now liberated; when, however, they meet in their nascent state, they again combine, forming alcohol. It is consequently a rule, and a highly important one to remember, that the yield of ether is continually smaller, in proportion to the water combined with the alcohol; that of 80 per ct., containing 20 per ct. of water, gives on distillation a far greater amount of spirit than ether, consequently it must not be employed.

The use of shaking the distillate with peroxide of manganese, is to convert the sulphurous acid into higher and odourless oxides (hyposulphuric and sulphuric acids), which, combining instantly with the protoxide of manganese formed, are on rectification left in the retort.

2 at. MnO_2 and 3 at. SO_2, form
1 at. $MnO + SO_3$ and 1 at. $MnO + S_2O_3$.

The lime employed at the same time combines with the sulphuric acid already present. On rectification, the ether being most volatile first passes over (containing only a trace of alcohol and water), then follows alcohol holding a little ether, and finally only hydrated alcohol. At the same time,

it happens that although the liquid before distillation is entirely neutral, the distillate will have an acid reaction. This phenomenon is explained by the behaviour of dry hyposulphates when heated, they are decomposed into sulphates and free sulphurous acid.

$$1 \text{ at. } MnO + S_2O_5, \text{ forms}$$
$$1 \text{ at. } MnO + SO_3, \text{ and } 1 \text{ at. } SO_2;$$

consequently, if any of the hyposulphate of oxide of manganese adheres to the sides of the retort, it will, by continued heating, be thus decomposed. This is easily remedied by employing only a charcoal fire, placed below only just the centre of the retort.

By shaking the officinal ether (which contains alcohol and water) with water, the alcohol is abstracted; but the ether at the same time acquires more water, to remove which it must be again rectified over chloride of calcium.

The sulphuric acid used in the preparation is afterwards available for many other purposes, as making pure sulphate of iron and sulphate of zinc.

Properties.—Ether is a transparent, thin, mobile fluid, of an agreeable penetrating odour and a cooling spirituous taste. It is highly inflammable, and the greatest care must be taken in keeping its vapour from contact with flame of any kind. The spec. grav. of the absolute is 0·720, of the officinal 0·740 to 0·750; the first being soluble in 10, the latter 9, parts of water,—both are miscible with alcohol in any proportion. It causes no alteration in the colour of litmus or turmeric paper. It is rapidly volatilized in an open dish, at the ordinary temperature, without leaving a residue; if an oily liquid remains, smelling of fusel oil and possessing a sharp taste, this arises partly from the employment of a very impure alcohol, and partly from the presence of a little oil of wine.

ÆTHER (PURUS) ALCOHOLATO-FERRATUS.

Spiritus Sulphurico Ethereus Martiatus.—Ferruginated Sulphuric Ether.—Bestuscheffsche's Nervine Tincture.

FORMULA: $C_4H_5O + xC_4H_6O_2$, HO, FeCl, ClH, C_4H_5Cl.

Preparation.—One part of crystallized chloride of iron (*Vide* FERRUM SESQUICHLORATUM) is dissolved in one part of distilled water, the solution shaken for one hour in a closed vessel with 4 parts of officinal ether, then allowed to remain quietly until two layers have formed; the upper one, of a golden yellow colour and equalling 5 parts, is decanted and mixed with 10 parts of alcohol, of 80 per ct. If required colourless, the tincture is put into small well-closed glasses, and placed in the direct rays of the sun until the colour disappears.

Recapitulation.—The chloride of iron combines, after some little time, with the ether, which it colours of a golden yellow. According to most pharmacopœias, the tincture, after the addition of the alcohol, should be bleached by exposing to the sun. This bleaching arises from the decomposition of the salt of iron; a portion of the chlorine being eliminated, protochloride of iron is formed, which is insoluble in ether but remains dissolved in the alcohol.

1 at. Fe_2Cl_3, forms
2 at. FeCl, and 1 at. Cl.

At the same time, the chlorine decomposes water in the sun light, hydrochloric acid being formed and oxygen eliminated.

1 at. Cl, and 1 at. HO, form
1 at. HCl, and 1 at. O.

The hydrochloric acid thus formed reacts on a portion of the alcohol present, separating from it the elements of two atoms of water, which it replaces, forming the so-called light muriatic ether.

1 at. $C_4H_6O_2$, and HCl, form
1 at. C_4H_5Cl, and 2 at. HO.

Whether, during the decolouration of the tincture, other products of decomposition are formed, which is not improbable, remains to be investigated.

Properties.—The tincture is a transparent, mobile fluid, of an agreeable ethereal odour and inky taste. Its spec. grav. is from 0·840 to 0·850. It reddens litmus paper powerfully. In bottles partially filled, and in a dark place, it becomes gradually green, then yellow; the protochloride of iron, by abstracting the chlorine from the muriatic ether, is converted into the perchloride, through the action of the oxygen of the air in the bottle, acetic acid and water being formed.

2 at. FeCl, 1 at. C_4H_5Cl, and 5 at. O, form
1 at. Fe_2Cl_3, 1 at. $C_4H_3O_3$, and 2 at. HO.

If sulphuretted hydrogen causes a blackening in the tincture, it contains copper, from the employment of impure chloride of iron.

ÆTHER ACETICUS.

Acetic Ether.—Acetate of Oxide of Ethyl.

Formula: $C_4H_5O + C_4H_3O_3 = Ae + \bar{A}$.

Preparation.—3 Parts of finely powdered sugar of lead are put into a glass retort, with a previously-cooled mixture of 1 part of concentrated sul-

phuric acid and 1 part of spirit of wine, 90 per ct. When the salt is thoroughly saturated and well shaken up with the spirit, the retort is placed in a sand bath, a receiver connected with it, but not quite air tight, by means of bladder, allowed to digest for a whole day with a very gentle heat, and then distilled to dryness. The acid distillate is shaken with some hydrate of lime, and, if it smells of sulphurous acid, with peroxide of manganese also; when neutralized, it is to be distilled until $\frac{1}{7}$ remains in the retort. The product will equal, or rather exceed, in weight, the alcohol employed.

The common acetate of soda (*vide* NATRUM OXYDATUM ACETICUM) may be advantageously employed for the process. To 1 part of concentrated sulphuric acid and 1 part alcohol, 90 per ct., are added 1 part acetate of soda and $\frac{1}{2}$ part of water. The acetate of soda and water are first put in the retort, and then the mixture of sulphuric acid and alcohol; then proceed as in the former process.

To prepare anhydrous acetic ether, the lead salt must first be deprived of its water of crystallization by a gentle heat, and added to the spirituous acid mixture. The acid distillate is then shaken with $\frac{1}{3}$ of its volume of water, and rectified over fused chloride of calcium.

Recapitulation.—By mixing the alcohol and sulphuric acid, exactly the same results occur as have been fully detailed under the head of ÆTHER PURUS; viz. bisulphate of oxide of ethyl is formed; when this comes in contact with acetate of lead, especially in the warm, an exchange of elements takes place, neutral sulphate of lead, neutral acetate of the oxide of ethyl, and free sulphuric acid resulting; the neutral acetate of oxide of ethyl is removed by distillation, leaving the sulphate of lead and sulphuric acid as a residue.

1 at. $(AeO + SO_3) + (HO + SO_3)$, and 1 at. $PbO + \bar{A}$, form

1 at. $PbO + SO_3$, 1 at. $AcO + \bar{A}$, and 1 at. $SO_3 + HO$.

2370 Parts of crystallized sugar of lead require, therefore, 1226 parts of hydrated sulphuric acid, and 640 parts of alcohol, of 90 per ct. In the quantities before given the salt and alcohol exceed this proportion, as the liberated sulphuric acid forms bisulphate of oxide of ethyl with the yet uncombined alcohol, and at the same time coming in contact with the remainder of the acetate of lead, a new portion of acetic ether is produced. The distillate is not a pure acetate of oxide of ethyl, but contains (dependent on the quantity of the acetate of lead and alcohol) water, alcohol, free acetic acid (formed by the action of a small portion of sulphuric acid on the sugar of lead; this cannot be obviated, but is reduced by the digestion and distillation to a mere trace), almost always sulphurous acid (*cide* the article ÆTHER PURUS), and free sulphuric acid, which latter, on the temperature increasing towards the end of the process, passes over. The residue, as previously noticed, contains sulphate of lead and free sulphuric acid. By agitating the distillate with lime and peroxide of manganese, the free acetic acid, sulphurous acid (partly converted by the oxygen of the manganese into sulphuric and hyposulphuric acids), and the sulphuric acid, combine with them, and are retained in the residue on rectification, whilst the neutral acetate of oxide of ethyl, with the alcohol and some water, passes over, and constitutes the officinal acetic ether.

The spirit is abstracted by shaking this with water, and the water by pouring off the ether which swims on its surface and distilling it with fused chloride of calcium.

The sulphate of lead formed may, after being treated with water to remove the free sulphuric acid, be used as a pigment.

By using the acetate of soda, exactly the same results are obtained, excepting that instead of sulphate of lead bisulphate of soda remains, which, when neutralized with lime, may be employed as Glauber's salts.

Properties.—Acetic ether is a transparent liquid, of a peculiar but agreeable and powerful smell and taste. Its spec. grav. is from 0·85 to 0·89; yet this is no proof of its strength, as with alcohol and water, in a certain proportion to the pure ether, its gravity may be as great as when free from either. The latter dissolves in 8, the former in 7 parts of water. If the acetic ether has a lower spec. grav. than 0·85, it contains free ether. It must not affect litmus and turmeric papers; it volatilizes readily and rapidly at a gentle temperature; if it leaves a residue which is blackened by sulphuretted hydrogen, lead is present.

One part of acetic ether and 3 parts of alcohol, 80 per ct., form the Spiritus aceticus aethereus.

ÆTHER MURIATICUS.

Chloric Æther.—Heavy Muriatic Ether.

FORMULA: $C_4H_4Cl_2$.

Preparation.—1 Part of common salt and 1 part of peroxide of manganese are thoroughly mixed, and put in a retort, into which is then poured a previously-cooled mixture of $2\frac{1}{2}$ parts concentrated sulphuric acid and $\frac{1}{2}$ a part of alcohol, of 90 per ct. The retort is placed in a sand bath, connected with a receiver, and its contents distilled to dryness. The acid distillate is digested

with milk of lime until, after several agitations, two layers form on standing; and when it no longer gives an acid reaction the lower one is drawn off, by means of a separation funnel, from the upper or watery layer; this, however, is sometimes reversed, the upper being the ethereal and the lower the aqueous solution, viz. when the new distillate requires much lime for its neutralization, and a specifically heavier solution of chloride of calcium is the consequence. When separated, it is rectified over half its weight of fused chloride of calcium. The product is small, at the most not exceeding $\frac{1}{4}$ of the salt employed. Prepared as commonly directed, still less is obtained from the employment of too much alcohol.

Recapitulation.—The mixture of sulphuric acid and alcohol consists, as stated under ÆTHER PURUS, in reality of bisulphate of oxide of ethyl, but contains also a considerable portion of free sulphuric acid; brought in contact with a mixture of peroxide of manganese and common salt (chloride of sodium) the manganese yields to the sodium half its oxygen, by which protoxide of manganese and soda are formed, $\frac{3}{4}$ of this combine with the free sulphuric acid present, and $\frac{1}{4}$ replaces the water of the 2 atoms of bisulphate of oxide of ethyl; forming two double salts, sulphovinate of soda and sulphovinate of manganese. These salts have but a momentary existence, for the chlorine liberated from the common salt instantly decomposes them into bisulphate of soda, neutral protosulphate of manganese, and free sulphuric acid, then separates from oxide of ethyl the elements of 1 atom of water and replaces them, forming with the other elements of oxide of ethyl, chloric ether, as follows:—

2 at. $C_4H_6O_2$ and 4 at. $SO_3 + HO$, form
2 at. $(AeO + SO_3) + (HO + SO_3)$ and 4 at. HO ;
then,
2 at. $(AcO + SO_3) + (HO + SO_3)$ 9 at. $SO_3 + HO$,
4 at. NaCl, and 4 at. MnO_2, form
3 at. $(NaO + SO_3) + (HO + SO_3)$, 3 at. $(MnO + SO_3)$, 1 at. $(AcO + SO_3) + (NaO + SO_3)$,
1 at. $(AeO + SO_3) + (MnO + SO_3)$, 8 at. HO, and 4 at. Cl ;
and,
1 at. $(AcO + SO_3) + (NaO + SO_3)$, 1 at. $(AcO + SO_3) + (MnO + SO_3)$, and 4 at. Cl, form
1 at. $(NaO + SO_3) + (HO + SO_3)$, 1 at. $MnO + SO_3$,
1 at. $(SO_3 + HO)$, and 2 at. $C_4H_4Cl_2$.

Altogether we require for the entire decomposition 2 at. alcohol, 12 concentrated sulphuric acid, 4 chloride of sodium, and 4 peroxide of manganese ; or 1280 parts of alcohol at 90 per ct., 7356 parts of hydrated sulphuric acid, 2932 chloride of sodium, and 2180 peroxide of manganese, which nearly agrees with the above relations, only that rather more manganese is ordered to allow for the impurities it contains, and a slight excess is not important. It must be expressly remarked that this process does not go on so evenly as above related, for the product which should at least equal the alchol used, is in fact only a fourth of it, and this arises from the formation of other products of decomposition, as Chloretheral, C_4H_4ClO ; Carbonic Acid ; Acetic Acid $= C_4H_3O_3$; Formic Acid, C_2HO_3, together with an ethereal substance, and a large proportion of Aldehyde $= C_4H_4O_2$; being so complicated as to render it difficult to give a stöchiometrical formula. I have therefore preferred noticing only the origin of the principal products. By the direct action of a small portion of sulphuric acid in common salt, free muriatic acid is formed ; this, together with other acids produced, is neutralized and removed by milk of lime, the water

of which also absorbs the alcohol and a great portion of the aldehyde: the whole of the latter however cannot be entirely removed. Chloride of calcium abstracts from it the last portion of water.

Properties.—Pure chloric ether is a colourless, oleaginous liquid, of an agreeable penetrating odour and aromatic taste, having a spec. grav. of 1·256. Alcohol and ether mix with it in every proportion, whilst water takes up only a small quantity. It must have no action on vegetable colours, and entirely volatilize when warmed.

ÆTHER NITROSUS.

Æther Nitricus.—Nitrite of Oxide of Ethyl.—Nitric Ether.

FORMULA: $C_4H_5O + NO_3 = AeO + NO_3$.

Preparation.—In a cylindrical vessel 6 or 8 times higher than wide are poured 10 parts of fuming nitric acid, spec. grav. 1·52; on this, taking care that the two fluids do not mix, 3 parts of water, and on the latter with the same precaution, 16 parts of alcohol of 90 per ct. The glass is tied over with moist bladder, having a small needle puncture in it, and set in a cool place, in summer in a vessel of cold water. The yellow colour of the acid gradually changes to green, then blue, and finally losing this the two lower layers are colourless, with the spirituous one above of a straw colour. So soon as this point is attained (possibly in about three weeks time), the upper yellow liquid is drawn off with a syphon and treated with milk of lime until it loses its acid reaction; it is then allowed to settle, the upper lighter yellow fluid is separated from the saline solution beneath, and rectified to about $\frac{1}{6}$ in an apparatus through which during the distillation a continuous stream of carbonic acid is passed. For this purpose, the exit

tube of the vessel in which the gas is washed is luted into the tubulus of the retort, the latter not having an air-tight connection with the receiver. The distillate should instantly be put into an air-tight bottle that must be quite full. It will equal about half the weight of the alcohol employed.

Recapitulation.—We have already shown under the article ÆTHER PURUS, that alcohol is a hydrate of oxide of ethyl, having the composition $C_4H_5O + HO$. Under ordinary circumstances nitric acid will not combine with this oxide (of ethyl), but losing 2 at. of oxygen, enters into combination with it as nitrous acid.

1 at. $C_4H_6O_2$ and 1 at. NO_5, form
1 at. $C_4H_5O + NO_3$, 1 at. HO, and 2 at. O.

These 2 latter atoms of oxygen are, however, not evolved free, but acting on another portion of alcohol abstracts from it 2 at. of hydrogen, forming 2 at. of water and a new body, the so-called aldehyde (dehydrogenized alcohol) $= C_4H_4O_2$.

1 at. $C_4H_6O_2$ and 2 at. O, form
1 at. $C_4H_4O_2$ and 2 at. HO.

For 788 parts of hydrated nitric acid 1280 parts of alcohol of 90 per ct. are requisite. The hyponitric acid $= NO_4$, in the fuming acid somewhat diminishes the quantity of aldehyde formed, as it has only to lose 1 at. of oxygen to become converted into nitrous acid. Besides nitric ether, aldehyde and water, Carbonic, Acetic, Formic, and Oxalic acids separate as secondary products. In order to prevent too violent an action of the acid on the alcohol they are separated by a layer of water and allowed to mix in the cold. The change of colour in the acid from yellow to green and then blue is owing to a portion of the hyponitric acid becoming converted into nitrous (having a blue appearance) and nitric acids on coming in contact with the water.

2 at. NO_4, form
1 at. NO_3 and 1 at. NO_5;

the blue nitrous acid and the yet unaltered yellow hyponitric acid form a green, allowing the blue to become apparent only on the entire decomposition of the latter acid.

The agitation with milk of lime is to effect the neutralization of free nitric acid, &c. The salts thus formed, with the free alcohol and most of the aldehyde, will then be retained by the water of the milk of lime. A portion of aldehyde, however, remains stubbornly combined with the nitric ether.* It is necessary to rectify it in an atmosphere of carbonic acid, otherwise the oxygen of the air in the apparatus would mix with it and cause the formation of free nitric acid.

Properties.—Nitric ether is a straw coloured fluid of a strong agreeable ethereal taste and smell, resembling apples. Its spec. grav. is 0·886. It is excessively volatile, more so than sulphuric ether, and boils at 70° Fah. It is soluble in 48 parts of water, and with alcohol in any proportion. It cannot long be kept without decomposition, rapidly acquiring when in contact with the air an acid reaction, by which nitric acid, acetic acid (from the aldehyde), and probably other products of oxidation also are formed.

ÆTHER NITROSUS ALCOHOLATUS.

Spiritus Nitro Etherius.—Spiritus Nitri Dulcis.—Spiritus Etheris Nitric.—Sweet Spirits of Nitre.

FORMULA: $(AeO + NO_3) + xC_4H_6O_2$, HO.

Preparation.—It is obtained by distilling a mixture of alcohol and nitric acid. 24 Parts of alcohol

* By passing the gas formed on boiling nitric acid with starch into alcohol, an ether containing aldehyde is still formed, the gas obtained in this case not being nitrous, but hyponitric acid.

80 per ct. (spec. grav. 0·840) are commonly prescribed to 6 parts of acid, spec. grav. 1·20. It is distilled in a sand bath or over a naked fire, until 20 parts have passed over; lime is then added and shaken with it so long as it reddens litmus paper; the neutral fluid poured from the excess of lime is now rectified to a small residue, and to exclude the external air the space between the retort and receiver must be tightly connected by bladder in which there are only a few needle punctures to allow the air contained in the receiver to escape. About 18 parts of sweet spirits of nitre are obtained, which must be at once put into 3 or 4 ounce bottles, well filled and stopped.

Recapitulation.—This is entirely the same as in the formation of nitric ether, viz., chiefly nitrite of oxide of ethyl and aldehyde are formed;

1 at. NO_5 and 2 at. $C_4H_6O_2$, form
1 at. $C_4H_5O + NO_5$, 1 at. $C_4H_4O_2$, and 3 at. HO,

which remain dissolved in the excess of alcohol. This preparation is distinguished from nitric ether by containing aldehyde (which is mostly separated from the latter by washing) as well as alcohol. Besides the secondary products named, ammonia is formed by the action of nitric acid on alcohol during the distillation, and remains combined with the acid in the retort; also hydrocyanic acid, which passes over, but is neutralized and separated on treating with lime. Of course the Cyanide of Calcium formed is decomposed in the subsequent rectification, but I have never found prussic acid in the distillate. The reason for keeping it in several small glasses is to prevent the whole stock from becoming acid at once from frequent exposure to the air.

Properties.—Spirit of nitric ether is an almost colourless (it has a slightly yellow tint) fluid of a similar taste and smell as the nitric ether, but less powerful, and a spec. grav. 0·840 to 0·850. By evapo-

ration with a gentle heat, it gives no residue. Its ready decomposition in contact with air is the reason of its acquiring in a short time an acid reaction in bottles not properly filled, nitric and acetic acids forming. When this has not proceeded far enough to give an effervescence with carbonate of potash, it is not worth noticing. If nitric acid containing muriatic has been used, the preparation will not be free from chloric ether, and this, when shaken with nitrate of silver, causes a white precipitate of chloride of silver, becoming violet on exposure to the light. Hydrocyanic acid will also cause, with a silver solution, a white precipitate, which, when heated to redness in a porcelain crucible, is decomposed into cyanogen and pure silver; this being entirely soluble in nitric acid may thus be separated from the insoluble chloride of silver.

ALDEHYDUM.

Alcohol dehydrogenatum.—Aldehyde.

FORMULA: $C_4H_4O_2$.

Preparation.—3 Parts of powdered peroxide of manganese, and 3 parts of concentrated sulphuric acid, previously diluted with 2 parts of water, are with 2 parts of alcohol of 90 per ct. poured into a retort, the latter placed in a sand bath, connected, but not quite air-tight, with a receiver to be kept quite cool, and distilled until $2\frac{1}{2}$ parts have passed over. The distillate is then rectified in a water bath with its own weight of anhydrous chloride of calcium to one half; and this is again repeated, so that now only $\frac{1}{2}$ a part of liquid is obtained. This last distillate is mixed with twice its volume of ether, and gaseous ammonia (obtained from equal parts of sal ammoniac and hydrate of lime) conducted into it

until it smells strongly of ammonia. During the absorption of the gas the liquid becomes turbid; after standing quietly for twelve hours in a well-closed vessel, the sides and bottom of the latter will be found covered with a quantity of colourless rhomboidal crystals; which increase on standing. It must, however, not be allowed to remain too long, otherwise the crystalline compound is again decomposed, but after from 8 to 14 days the mother liquor is poured off the crystals; the latter are washed a few times with ether, dried between blotting paper, dissolved in their weight of water, the solution poured into a retort already containing a cooled mixture of $1\frac{1}{2}$ parts of sulphuric acid (to 1 part of crystals) and 2 parts of water, the retort placed in a water bath connected with a receiver, and gently warmed; so soon as the water in the bath boils the distillation must be discontinued. The distillate, hydrated aldehyde, must be rectified from its own weight of fused chloride of calcium. In order to prevent too strong a heat from occurring when the hydrated aldehyde comes in contact with the fused chloride of calcium, and thus occasion a loss, the fused salt is first placed in a tubulated retort, luted to a receiver, the retort placed in cold water, ice, or snow, and the liquid poured in small portions through a long-necked funnel, fitted to the tubulus of the retort with a cork; the tubulus is then entirely closed, the retort placed in a water bath and warmed very gently. A second rectification from chloride of calcium will remove the last trace of water. The yield is very trifling. I obtained only $\frac{1}{24}$ of the weight of alcohol used.

Recapitulation.—By the combined action of sulphuric acid, peroxide of manganese and alcohol, several products result, principally however the so-called aldehyde; the oxygen of the manganese, which is liberated by the sulphuric acid, combines with 2 at. of hydrogen of the alcohol to form water,

the other elements of the alcohol constituting aldehyde.

2 at. MnO_2, 2 at. SO_3 and 1 at. $C_4H_6O_2$, form
2 at. $MnO + SO_3$, 2 at. HO, and 1 at $C_4H_4O_2$.

The other secondary products, which invariably accompany this decomposition of the alcohol, are Carbonic acid, Formic acid, Formic ether, Acetic acid, Acetic ether, and traces of pure ether. The raw distillate is distilled several times over chloride of calcium, to abstract the water, and to remove these other compounds it is treated with ammonia, with which it forms a crystalline compound ($NH_3 + C_4H_4O_2$). The ether is employed to prevent the too ready absorption of the gas, and the formation of a crystalline pasty mass which would render its entire saturation difficult. From the above compound sulphuric acid separates aldehyde which distils, and forms bisulphate of ammonia, which remains behind. Finally, chloride of calcium frees the aldehyde from adhering water.

Properties.—Pure aldehyde is a colourless mobile fluid, of a spec. grav. 0·790, boiling at 71° Fah., and possessing a peculiar penetrating ethereal odour. It mixes in every proportion with water, alcohol, and ether; has neither an acid nor an alkaline reaction; and in contact with oxygen (as when kept in vessels only partially full) is converted gradually into acetic acid and water.

1 at. $C_4H_4O_2$ and 2 at. O, form
1 at. $C_4H_3O_3$ and 1 at. HO.

ALCOHOL (PURUM).

Absolute Alcohol.—Anhydrous Alcohol.

FORMULA: $C_4H_6O_2$.

Preparation.—A copper still, having a tin head and worm pipe, is three parts filled with spirits of wine, of about 80 per ct., as obtained at distillers; to this is added, during constant stirring with a wooden stirrer, one-third of its weight of fused coarsely-powdered chloride of calcium, and, after well luting on the head, distilled with a gentle fire until seven-eighths of the spirit has passed over; the receiver is now changed, and the fire kept up whilst the distillate has a spirituous taste, which cannot be very long. If the last portion should be as strong as the first seven, of course it may afterwards be mixed with them.

To the stronger alcohol thus obtained is added, in the same manner, one-half of its weight of coarsely-powdered fused chloride of calcium, and distilled; when one-seventh has passed over change the receiver, and again when five-sevenths have distilled, then continue the fire until only water is obtained. The first and third portions will be of about 97—98 per ct.; the second and largest portion will be anhydrous. 8 Parts of alcohol, of 80 per ct., yield about 5 parts of anhydrous.

Recapitulation.—The use of the fused anhydrous chloride of calcium, =CaCl, in dehydrating the spirit, consists in the property which it possesses of combining with 2 at. of water with such force that they can only be expelled at a red heat. One would suppose that with a larger quantity of chloride of calcium the whole of the water should be abstracted by one distillation; this, however, is not the case, it being necessary that the spirit shall first

reach a particular strength before it will part with its last atom of water. The first portion of the distillate is alcohol, of 90 per ct. (spec. grav. 0·818), which is applicable to many purposes, as the manufacture of ether, &c. We will now endeavour theoretically to explain the formation of alcohol of 90 per ct. by the distillation of that at 80 per ct., with one-third of chloride of calcium. 20 Per ct. water in alcohol is equivalent to $1\frac{1}{3}$ atoms; the composition of such an alcohol may therefore be expressed as $=3C_4H_6O_2+4HO$. To take up half this water, viz. 2 at., requires 1 at. chloride of calcium, whilst spirit, still combined with 2 at. of water, remains.

3 at. $C_4H_6O_2$, 4 at. HO, and 1 at. CaCl, form
1 at. $CaCl+2HO$, 3 at. $C_4H_6O_2$, and 2 at. HO.

2160 Parts of 80 per ct. alcohol require, for this purpose, 693 parts of chloride of calcium, or to 3 of the first 1 of the latter. To abstract the other 10 per ct. by a second distillation an excess of chloride of calcium is required, in order to overcome the affinity existing between alcohol and water. Now, however, occurs a peculiarity which makes it necessary to divide the second distillate. Absolute alcohol boils at 168·36° Fah., alcohol of 97 or 98 per ct. at 168·08° Fah.; consequently the first or most volatile portions cannot be anhydrous, and unless this precaution of separating the first portion of the distillate be attended to, no quantity of the chloride of calcium will ensure an anhydrous product. Of the range between 94 and 100 per ct., alcohol of 97 or 98 per ct. is the most volatile, absolute alcohol not being more volatile than that at 94 per ct.; and it is only the still greater affinity of chloride of calcium for water that causes the alcohol to yield it up to it.

Properties.—The most important test of spirit of wine is its content of anhydrous alcohol, which is

learned from its specific gravity. Anhydrous alcohol has a spec. grav. of 0·792; it is only to be obtained of this strength by repeated treatments with chloride of calcium, and as it attracts water with the greatest avidity, must be kept in bottles very carefully closed. The spec. grav. of the alcohol of 98—99 per ct. is 0·798. Should the distillation have been too violent, a portion of the chloride of calcium may have been carried over by the vapour of the alcohol, in which case the distillate will yield, with nitrate of silver, a white precipitate of chloride of silver, becoming, by exposure to the light, of a violet colour. It may also contain the ordinary impurities of spirit of wine and brandy, as Fuselöl, Acetic acid, or Copper. *Fuselöl*, which forms during the fermentation of the corn or potatoes, and exists in all raw spirit, is known by its highly repulsive odour, that is perceptible on rubbing the spirit between the hands. The alcohol of the spirit evaporates first, and thus no longer masks the scent of the fuselöl. This alcohol mixed with much water becomes turbid from the separation of the fuselöl, and in such a mixture the smell of fuselöl is far more readily perceptible than in the alcohol alone. A still more certain method of detecting it is, to add a few drops of caustic potash to two or three ounces of alcohol, evaporate slowly to about a quarter of an ounce, and add to this residue a little drop or two of dilute sulphuric acid; the penetrating odour of the fuselöl will now be evident, should any be present. The caustic potash combines with the fuselöl, and prevents it evaporating with the alcohol; from this combination it is set free by the sulphuric acid. A reddish colour, on the addition of nitrate of silver to alcohol (arising probably from the reduction of silver), is also a sign of the presence of fuselöl. *Acetic acid* arises from the oxydation of the alcohol whilst very dilute and exposed to a temperature above that of

the atmosphere; it will also generally be formed with fuselol, during the fermentation. If ever so small a quantity of acetic acid is present, not enough to colour litmus red, yet on adding to a few ounces of alcohol some grains of carbonate of lime, evaporating at a low temperature, almost to dryness, and adding a few drops of concentrated sulphuric acid, the smell of acetic acid is instantly evolved. *Copper* is found in the alcohol when the latter contains free acetic acid and has been distilled in an apparatus with a copper worm. If this is the case, the alcohol, after concentrating considerably by evaporation, will yield, with ferrocyanide of potassium, a reddish colour, or a chocolate-coloured turbidity; (*Vide* ACID. ACET.)

Additional Remarks. — The different spirits of wine in most common use are arranged according to their degree of concentration, as follows:—

1.—Absolute or Anhydrous Alcohol; Alcohol Absolutum, spec. grav. =0·792—0·798.
2.—Alcohol of 90 per ct.; Spiritus Vini Alcoholisatus, spec. grav. =0·818.
3.—Alcohol of 80 per ct.; Spiritus Vini Rectificatissimus, spec. grav. 0·840.
4.—Alcohol of 60 per ct.; Spiritus Vini Rectificatus, spec. grav. 0·880.
5.—Alcohol of 40 per ct.; Spiritus Frumenti, spec. grav. 0·925.

ALUMINUM OXYDATUM SULPHURICUM.

Argilla Sulphurica.—Alumina Sulphurica.—Sulphate of Alumina.

FORMULA OF THE ANHYDROUS: $Al_2O_3 + 3SO_3$.

FORMULA OF THE CRYSTALLIZED: $Al_2O_3 + 3SO_3 + 18HO$.

Preparation.—3 Parts of alum are dissolved in 60 parts of warm water, Liquor ammonia is added to

the solution, when cool, so long as a precipitate forms, (about 2 parts of ammonia, of spec. grav. 0·960); the liquid is freed from the adhering salts by decantation, placed on a linen strainer, afterwards in a porcelain dish, warmed, and, with stirring, dilute sulphuric acid is added to the pasty mass until it is entirely dissolved; for this purpose rather more than $3\frac{1}{3}$ parts of dilute acid are requisite. If necessary the solution is filtered, and either crystallized, or, as this is somewhat difficult, slowly evaporated to dryness in a sand bath. It yields rather more than 2 parts of crystallized or 1 of dried sulphate of alumina.

Recapitulation.—Alum (we will in this case take potash alum) is decomposed by caustic ammonia, so that the alumina separates, combined, however, with 1 at. of sulphuric acid and 9 at. of water, 2 at. of sulphate of ammonia being formed, which remain with the sulphate of potash of the alum, in solution.

1 at. $KO + SO_3Al_2O_3 + 3SO_3$, 24HO, and $2NH_3$, form
1 at. $Al_2O_3 + SO_3 + 9HO$, 2 at. $NH_4O + SO_3$, 1 at. $KO + SO_3$, and 13 at. HO.

5932 Parts of alum require 426 parts of anhydrous, or 4260 parts of hydrated ammonia, of 0·960 spec. grav. (containing about $\frac{1}{10}$ of anhydrous) for its decomposition. In order to re-dissolve this precipitate, $Al_2O_3 + SO_3 + 9HO$, 2 at. of sulphuric acid, = 1000 or 1225 hydrated sulphuric acid ($SO_3 + HO$), or 7350 dilute sulphuric acid (containing $\frac{1}{6}$ of hydrate of sulphuric acid) are necessary.

Properties.—Neutral sulphate of alumina crystallizes with difficulty, forming white, shining, pearly plates, which are odourless, of a sweetish astringent taste, and soluble in 2 parts of water. Dried, it forms a white crystalline powder, which does not abstract moisture from the air, and requires

rather more than 4 parts of cold water for its solution. The crystallized salt when warmed fuses in its water of crystallization which gradually evaporates, whilst at a higher temperature (red heat), the sulphuric acid also is evolved leaving pure alumina. Its solution must give no precipitate with chloride of barium nor a blue one with ferrocyanide of potassium; the first would be due to *sulphuric acid*, the latter to *iron*. Besides these impurities, it may, if not carefully washed, also contain *ammonia* which is readily detected by the smell evolved when treated with caustic potash solution. *Potash* is detected by precipitating with excess of ammonia, filtering, evaporating the solution to dryness and heating to redness: any residue is then treated with water, filtered and supersaturated with tartaric acid when potash would yield a crystalline granular precipitate of bitartrate of potash.

AMMONIACUM CAUSTICUM AQUOSUM.

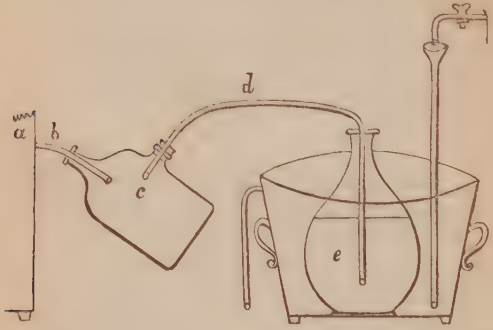
Liquor Ammonii Caustici.—Caustic Ammonia.—Liquor Ammonia.—Solution of Ammonia.

FORMULA: $NH_3 + xHO$.

Preparation.—In a copper still, having a tin head and worm, are placed 3 parts of burnt lime, which is then sprinkled with 1 part of common water; the still is now covered until the lime has slaked and cooled, after which, 3 parts of coarsely powdered sal ammoniac and 2 parts of water are added, and the whole well stirred up with an iron spatula until a uniform pasty mass is obtained; the head is then adjusted and well luted. To the exit hole of the worm is tightly fixed, by a double bladder, a tubulated bottle or flask (or a Wolf's bottle), in the tubulus of which, by means of a perforated cork, is fixed a leaden pipe, the other end of which reaches

nearly to the bottom of a glass globe containing 4½ parts of distilled water, and connected, but not quite air-tight, by means of bladder. The globe is placed in a tub or other suitable vessel, fire applied to the still, and so soon as the evolution of gas commences a constant stream of water is passed, by means of a metal pipe, to the bottom of the tub; the heated warm water escaping over the upper edge.

The apparatus is depicted in the following woodcut;



(*a*) is the worm tub, (*b*) the exit end of the worm, (*c*) the tubulated receiver, &c. Together with the gas, some solution of ammonia will escape and be collected in (*c*). The greatest attention must be paid to the fire which should on no account be withdrawn, otherwise the liquid in globe (*e*) will quickly be absorbed into the flask (*c*). When the gas passes over more slowly, the fire is somewhat increased, and on no more bubbles appearing, the leaden tube is withdrawn from the globe and placed

n a bottle containing from ½ a pound to 1 pound of distilled water; the fire is continued until the contents of the flask (*c*) equals from 1½ to 2 parts. The contents of the globe mixed with so much distilled water as will bring it to a spec. grav. 0·960 will be about 7½ parts, and that in the receiver (*c*) brought to the same spec. grav. about 2½ parts; the two liquids are not mixed, that in (*e*) being the purest; the contents of (*c*) are generally turbid, but become bright on standing, and may be decanted from the deposit formed.

Instead of a copper still, a cast-iron pflanched pot may be employed, on which is fixed by means of screws, an iron cover with a short iron tube fitted in it, which may be lengthened by means of a lead pipe. If the ammonia is required only in small quantities, the lime may be slaked with half its weight of water in an iron pot, quickly mixed with the powdered sal ammoniac, put into a flask, the latter placed in a sand bath, connected with a leaden or glass tube, and the process conducted as above.

Recapitulation.—Sal ammoniac consists of an equivalent of ammonium (NH_4) and chlorine = NH_4Cl. Lime (oxide of calcium = CaO) decomposes it, forming chloride of calcium, water, and ammonia.

1 at. NH_4Cl and 1 at. CaO, form
1 at. CaCl, 1 at. HO, and 1 at. NH_3.

668 Parts require only 350 parts of lime, but equal parts are prescribed, as in the first place the lime may not be quite pure, and the excess will also insure a more certain contact with the sal ammoniac; for this reason more water is ordered than is necessary to slake the lime, viz. sufficient to convert the whole into a thick paste. The slaking of the lime (which is thus converted in a convenient manner into an extremely fine powder) is due to the avidity with which this base combines with 1 at. of water, forming a hydrate.

1 at. CaO and 1 at. HO, form
1 at. CaO + HO;

consequently 350 parts of lime require 112 parts of water or 3 parts of the former, 1 part of the latter. The heat thus generated is partly owing to the water passing from the fluid to the solid state, and also from the great affinity lime has for it. In order to obtain most of the gas entirely pure, two receivers must be employed, and, on account of the fragility of glass tubes, they are connected without any prejudicial results, by means of a leaden one. It is necessary to keep the receiver (*e*) well cooled otherwise a considerable loss of ammonia will ensue as much heat is evolved during its passage from the gaseous to the liquid state. The proportion which solution of ammonia bears to the sal ammoniac employed is explained by the following consideration:—668 parts of sal ammoniac contain 213 parts of ammonia (NH_3), or 3 parts of the former, nearly 1 part of the latter. The solution of ammonia spec. grav. 0·960 contains in 100 parts 90·4 water and 9·6 ammonia, consequently 10 parts contain nearly 1 part of pure ammonia. The evolution vessel will contain chloride of calcium and hydrate of lime, on account of the excess of lime employed; or, speaking more correctly, of neutral chloride of calcium, basic chloride of calcium ($CaCl + 3CaO$), and water. It may be used as chloride of calcium, as on boiling with water the chloride of calcium and a little free lime remain dissolved, and hydrate of lime precipitates.

Properties.—Pure Liquor ammonia is a transparent liquid of a peculiarly pungent smell and caustic taste. Turmeric paper is quickly and strongly browned by it, but regains its yellow colour on exposure to the air. The above strength, of spec. grav. 0·960, is the most useful. If required stronger, the contents of the receiver must be diluted in proportion. On

account of its volatility it must be kept in bottles with well-fitted glass stoppers (corks are changed to a brown colour and gradually corroded by it), and in a cool place. At a gentle heat it is entirely volatile, any residue will be an impurity. That in the receiver (*e*) will, generally speaking, be chemically pure, and only occasionally contaminated with a trace of *sal ammoniac*, which may be detected by the addition of a drop of solution of nitrate of silver, and supersaturation with nitric acid otherwise the chloride of silver will remain dissolved. The solution in the first receiver is almost always turbid with in general a yellow tinge. The colour generally arises from traces of volatile oil in the sal ammoniac, and may be removed by agitation with fresh wood charcoal.

The turbidity may be from mechanical admixture with lime or oxide of tin. The lime is generally found in the precipitate as carbonate and is formed when the ammonia has absorbed carbonic acid by mutual decomposition with any chloride of calcium that has been carried over, muriate of ammonia remaining in solution: and in this case the addition of oxalate of ammonia to the solution will generally cause a precipitate and prove the existence of undecomposed chloride of calcium. If after filtering off the oxalate of lime phosphate of soda is added, another precipitate, of ammonio phosphate of magnesia, will in all probability be obtained, as ordinary lime is seldom quite free from magnesia. The latter precipitate ensues as follows:

2 at. MgCl, 1 at. 2 $NaO + HO + P_2O_5$, 1 at. NH_3, and 13 at. HO, form
2 at. NaCl. and 1 at. 2 $MgO + NH_4O + P_2O_5 + 13$ HO.

Previously to testing for magnesia, the lime must be removed by the oxalate of ammonia, otherwise it would mislead by giving a precipitate with phosphate of soda. The oxide of tin which arises from

the use of a tin head and worm is the principa cause of the turbidity of the contents of the receiver (*c*); when not carefully kept out of contact with air and moisture these vessels gradually acquire a thin coating of suboxide of tin on their inner surface, the vapours of ammonia passing over this, decompose it into oxide of and metallic tin, the former of which it carries with it, together with small portions of lime; but the oxide of tin not being soluble in the ammonia liquor remains only in suspension, and after standing a few weeks is deposited (with carbonate of lime) so thoroughly, that the supernatant liquid may be poured off quite clear. This precipitate I never found to exceed 2 grains from as much as 15 or 20 pounds. As well as oxide of tin such an ammonia will contain *protoxide* of *tin* dissolved, the fear of its containing metallic tin (dissolved) is groundless. If the solution of ammonia has a bluish tint, *oxide* of *copper* is contained; this can happen only occasionally, and from employing too strong a fire. Hydrosulphate of ammonia in this case causes a black turbidity or precipitate of sulphuret of copper, and by adding this reagent very carefully, the whole of the copper may be removed by deposition and filtration. When not carefully excluded from the air the ammonia will contain *carbonic acid*, which on shaking with baryta water will cause a white turbidness (carbonate of baryta). If, instead of distilled, common water has been used, of course the ammonia will contain its impurities, amongst others, sulphuric acid, which causes with chloride of barium a white precipitate insoluble in hydrochloric acid.

AMMONIUM CHLORATUM DEPURATUM.

Ammoniæ Hydrochloras—Flores Salis Ammoniaci.—Purified Sal Ammoniac.

FORMULA: NH_4Cl.

Preparation.—Any convenient quantity of sublimed muriate of ammonia, broken in small pieces, is digested in a porcelain dish, with one and a half times its weight of distilled water, and heated over a free charcoal fire. As soon as the salt has dissolved, ½ an ounce of caustic liquor ammonia is added for every pound of it, then heated a short time, filtered through a linen strainer covered with filtering paper, and with constant stirring evaporated to dryness, at a gentle heat.

Recapitulation.—The only impurity generally found in sublimed sal ammoniac is a little iron, arising from the use of iron subliming vessels, and the formation of a volatile chloride of iron. The chloride of iron during the sublimation is decomposed into an acid and a basic salt, the first of which dissolves with the sal ammoniac, the last remains; consequently, all the iron is not removed by simply dissolving and filtering, but the addition of some ammonia is necessary, which decomposes the chloride of iron, forming sal ammoniac and insoluble hydrated oxide of iron, which remains on the filter. As sal ammoniac forms no well-defined crystal, and also has a disagreeable propensity of creeping over the sides of the vessel, it is best to evaporate it to dryness. (This creeping of the fluid over the edges of the dish is caused by the formation at the edge of the solution of a number of rows of very fine crystals, which form a series of channels, that, by capillary attraction, absorb the liquid, which produces on the upper edge, by exposure to

the air, other rows of crystals, these again act similarly, increasing the length of the capillary tubes, and this only ceases with the supply of fluid). Metal vessels must be carefully avoided.

Properties.—The purified sal ammoniac is a snow-white crystalline powder consisting of a number of very small cubes and octohedrons; is odourless, of a sharp saline taste, soluble in 2½ parts of cold, and in 1 part of boiling water; it dissolves, but not quite so readily, in alcohol; it has a faintly acid reaction, which, as with many other salts of ammonia, arises from the evolution of a small quantity of the base during evaporation. It is entirely volatilized on heating; if it contains *iron*, its solution gives with tannin a violet or bluish turbidity of tannate of iron. The commercial salt also may contain *sulphate of ammonia*, which, though volatilized by heat, gives rise to the formation of sulphurous acid, water, ammonia, and nitrogen.

3 at. $NH_4O + SO_3$, form
3 at. SO_2, 6 at. HO, 2 at. NH_3, and 1 at. N.

If, therefore, we sublime the salt in a retort connected with a receiver, and the latter afterwards contains water, having the odour of burning sulphur, we may be sure that sulphate of ammonia was present. It can also be detected by addition of chloride of barium to the solution; but the sulphuric acid may be combined with other bases, as with lime (which will cause a precipitate with oxalate of ammonia), or magnesia (which, after the removal of the lime, is detected by phosphate of soda and ammonia); in which case it forms, together with sulphate of soda, insoluble ammonio-phosphate of magnesia.

2 at. $MgO + SO_3$, 1 at. $2NaO + HO + P_2O_5$,
1 at. NH_3, and 13 at. HO, form
2 at. $NaO + SO_3$, and 1 at. $2MgO + NH_4O + P_2O_5 + 13HO$.

Soda may also be present as *sulphate*, or as *chloride* of *sodium*; to determine this, dissolve the residue after sublimation, filter if necessary, and evaporate slowly, when the chloride of sodium will crystallize out in cubes, the sulphate of soda in long oblique rhombic prisms, which heated in the blowpipe flame impart to it an intense yellow colour. Other metals besides iron may be contained; *lead*, for instance, which gives a white precipitate with sulphuric acid; *copper*, which is known by the blue colour it causes with ammonia, or by its forming a deposit of metallic copper on clean bright iron, an equivalent of the latter being dissolved in its stead. Traces of empyreumatic oil, which are seldom absent in the best sal ammoniac, and come from the carbonate of ammonia used in its preparation, are detected by treating the sal ammoniac with lime, and collecting the gas in water, to which, if present, they impart a yellow colour; (*Vide* AMMONIACUM CAUSTICUM).

AMMONIUM CHLORATUM FERRATUM.

Ferri Ammonio Chloridum.—Flores Salis Ammoniaci Martialles.—Ammonio Chloride of Iron.

FORMULA: $NH_4Cl + xFe_2Cl_3$.

Preparation.—4 Parts of crystallized chloride of iron (*Vide* FERRUM SESQUICHLORATUM) and 15 parts of sublimed sal ammoniac are dissolved in a porcelain dish with 40 parts of hot distilled water, and the solution, with constant stirring, is evaporated until concentrated over a naked fire, and then to dryness on a sand bath. The salt whilst warm is rubbed up, put into well-closed bottles, and in a dark place.

The proportions vary according to different phar-

macopœias (the above is the Bavarian, and consists of about 15 at. of chloride of ammonium to 1 of chloride of iron); the necessary quantity of chloride of iron is readily determined when we mention, that the latter contains, in its crystalline state, $\frac{1}{4}$ its weight of metallic iron.

Recapitulation.—Between the chlorides of iron and ammonium there is little affinity toward the formation of a double salt; consequently the preparation can scarcely be considered more than a mixture of the two salts. If evaporated to crystallization, at first, small slightly yellow crystals of chloride of ammonium form, containing but little iron; each succeeding crystallization is of a deeper colour, the chloride of iron being much the most soluble; consequently, in order to acquire a uniform preparation, it is necessary to rub the several crystallizations well together; it is better and easier, therefore, at once to evaporate the solution to dryness, which, when the mass becomes thick, must only be carried on in a sand bath and with constant stirring, otherwise the chloride of iron will sink to the bottom, and from the action of the water be partially converted into free acid and basic chloride.

3 at. Fe_2Cl_3, and 6 at. HO, form
1 at. $Fe_2Cl_3 + 2Fe_2O_3$, and 6 at. HCl.

In this case the preparation no longer forms a clear solution in water, but leaves some yellowish-brown flakes undissolved.

In the light it gradually becomes paler, and must consequently be kept in a dark situation. This bleaching is due to action of the rays of light, which, at the expense of the adhering water, reduce a portion of the perchloride to protochloride of iron.

1 at. Fe_2Cl_3, and 1 at. HO, form
2 at. FeCl, 1 at. ClH, and 1 at. O (which is evolved).

Properties.—The ammonio chloride of iron is an orange-yellow crystalline powder, with a saffron-like smell and a sharp, saline, astringent taste; it attracts moisture from the air, and dissolves in $2\frac{1}{2}$ parts of water. The solution has an acid reaction. If it leaves a dense yellowish-brown residue on solution, the heat employed at the end of the process was too great; but as it is almost impossible to avoid the decomposition of a small quantity of the chloride of iron, a slight insoluble residue must always be expected. If it has long been exposed to the light, it may also contain protochloride of iron, in which case ferridcyanide of potassium will cause in the solution a deep-blue precipitate, a combination of 1 at. of ferridcyanide of potassium and 4 at. of a Prussian blue, consisting of 3 at. of protocyanide of iron and 1 at. of percyanide.

12 at. FeCl, and 5 at. $3KCy + Fe_2Cy_3$, form
12 at. KCl, and $(3KCy + Fe_2Cy_3) + 4(3FeCy + Fe_2Cy_3)$.

Other impurities may be determined, as in sal ammoniac.

AMMONIUM IODATUM.

Ammonii Iodidum.—Hydriodate of Ammonia.—Iodide of Ammonium.

Formula: NH_4I.

Preparation.—Into a glass flask capable of holding 20 parts of water, are put 1 part of fine iron filings, 8 parts of distilled water, and gradually 4 parts of iodine, in small portions. The iron combines with the iodine and heat is evolved. So soon as the liquid loses its brown and acquires a green colour, it is filtered and mixed with 2 parts of iodine; when these are dissolved, solution of ammonia is

added so long as a precipitate is caused (for this 8 parts, or rather more, are necessary), it is filtered again, and, with constant stirring, gently evaporated to dryness, in a porcelain dish, on a sand bath.

Prepared as above, the salt is of a pale-yellow colour; it should, however, be white, and to obtain it thus it is necessary to triturate it for some time at a gentle heat, and when the colour has disappeared put it, whilst still warm, in a well-closed bottle. It will weigh about 6½ parts.

Recapitulation.—The iodine combines with the iron (which in the proportion directed is in excess) to form proto-iodide, =FeI. In the dry state their combination is but imperfect. The only part the water plays is to facilitate the process, and in describing this it is by no means necessary to consider that water is decomposed, giving its oxygen to the iron and its hydrogen to the iodine, whilst hydriodic acid, reacting on the protoxide of iron, forms protoiodide of iron and water, thus:—

1 at. HO, 1 at. Fe, and 1 at. I, would form
1 at. FeO + HI = 1 at. FeI, and 1 at. HO.

But according to the proposition "corpora non agunt nisi fluida," it is necessary for their combination that one of them first assumes the fluid state. And it thus takes place:—at first a little iodine dissolves in the water, and *then* combines with a portion of the iron, forming a solution of proto-iodide of iron, which is capable of dissolving far more iodine than pure water, and thus acquires a greater power of acting on the iron than at first, and this continues progressively until all the iodine is taken up, if iron is in excess. 1 At. of iodine, =1586 parts, requires really only 1 at. of iron, =350 parts; it is, however, always better to use rather more (say ¼ its weight) of iron. The iodine must not be added at once, or the heat will be aised so much as either to break the glass or cause

the fluid to boil over. If we add to the proto-iodide half as much iodine as it already contains, we form per-iodide:—

2 at. FeI, and 1 at. I, form
1 at. Fe_2I_3;

and on the addition of solution of ammonia the peroxide of iron is precipitated as a hydrate, the readily-soluble iodide of ammonium being formed.

1 at. Fe_2I_3, 3 at. NH_3, and 6 at. HO, form
1 at. $Fe_2O_3 + 3HO$, and 3 at. NH_4I.

The proto-iodide of iron, previously to its decomposition with ammonia, is converted into per-iodide, because from the latter the whole of the iron can be precipitated, but from the former protoxide of iron would be thrown down, which is slightly soluble in the ammonia salt formed, as well as in excess of ammonia.

The affinity between iodine and ammonia is but feeble, and even during its evaporation a slight decomposition takes place, a portion of the salt separating into ammonia and hydriodic acid.

1 at. NH_4I, forms
1 at. NH_3, and 1 at. HI.

The ammonia passes off, but the hydriodic acid, losing some of its hydrogen and forming hydriodous acid (Hydriodic acid + Iodine = HI_2), remains partially combined with the salt, imparting to it a yellow colour. Addition of ammonia neither prevents nor obviates this (as it converts the hydriodous acid into iodide of ammonium and free iodine); for the entire removal of the hydriodous acid it is necessary to warm the salt for some time, when in its dry state.

Properties.—Pure iodide of ammonium forms a white crystalline powder, in reality odourless, but from a very slight exposure to the air it acquires a

scent of iodine; it has an iodized, strongly saline taste. It is extremely soluble in water; its solution slowly evaporated, slightly reddens litmus, and yields cubical crystals. In the air it attracts moisture, and undergoes the same decomposition as by evaporation, viz. it evolves ammonia; the solution acquires first a yellow then a brown tint, and forms hydriodous acid, with a smell of iodine. The salt must, therefore, be kept in well-closed bottles.

AMMONIUM OXIDATUM ACETICUM LIQUIDUM.

Liquor Ammoniæ Acetatis.—Spiritus Mindereri.—Solution of Acetate of Ammonia.—Mindererus's Spirit.

Formula: $NH_4O + C_4H_3O_3 + xHO$.

Preparation.—In making this the pharmaceutist must take care to employ the proportions directed in his own Pharmacopœia, as all do not order a liquor of a similar strength, that is, containing the same weight of dry acetate of ammonia. Consequently, we can only offer here some remarks in reference to its formation. There are two methods of proceeding, either to neutralize strong acetic acid with dry carbonate of ammonia, and in case water is to be added taking care that it corresponds to the carbonate of ammonia employed; for instance, to 1 ounce of the latter add sufficient water to make the whole up to 16 ounces; or, another method is, to exactly neutralize liquor ammonia with concentrated acetic acid, both being of the strength directed (as determined by their spec. grav.). There are two evils in the first method; the ordinary sesquicarbonate of ammonia suffers gradual decomposition, if it is not always most carefully

guarded from exposure to the air (which is scarcely practicable), into neutral carbonate (evolved) and bicarbonate of ammonia (which remains), finally becoming a white powder; (*Vide* AMMONIUM CARBONICUM). It may still retain its shape in hard lumps, and yet be entirely converted into bicarbonate. Of course the bicarbonate of ammonia contains less ammonia than the sesquicarbonate, the liquor consequently will be too weak. Then it is necessary, in order entirely to get rid of the carbonic acid, to warm the liquid, which tends to cause its more speedy decomposition.

The second method is unsatisfactory if the real acetic acid is calculated from the spec. grav. of that employed, this not being a just criterion of its strength.

The best method is to calculate the strength of the Liquor ammonia acetatis from the quantity of acetic acid employed, the strength of which is determined, not by its spec. grav., but from the quantity of dry carbonate of potash or soda it has been previously found to neutralize. 865 Parts of dry (anhydrous) carbonate of potash, or 665 parts of dry carbonate of soda, correspond to 638 parts of anhydrous acetic acid.

If the strength of the acetic acid is once thus established, it is quite immaterial what proportion of carbonate or Liquor ammonia is required to neutralize it, as a sufficient quantity of water to bring it to the proper strength may then be added.

Recapitulation.—Ordinary carbonate of ammonia consists of 2 at. of oxide of ammonium, and 3 at. of carbonic acid, $=2NH_4O + 3CO_2$; the acetic acid drives out and replaces the carbonic acid.

1 at. $(2NH_4O + 3CO_2)$, and 2 at. $C_4H_3O_3$, form 2 at. $NH_4O + C_4H_3O_3$, and 3 at. CO_2.

1475 Parts of carbonate of ammonia require 1276

parts of anhydrous, or 3544 parts of acetic acid, containing 64 per ct. water; (*Vide* ACIDUM ACETICUM). The carbonic acid can only be entirely driven off by heat, which must not however be too great, otherwise acetate of ammonia will be volatilized.

100 Parts of caustic liquor ammonia, spec. grav. 0·960 (containing nearly 10 per ct. anhydrous ammonia) require about 30 parts of anhydrous or 85 parts of acetic acid, of the strength ordered. The ammonia in this instance simply combines with the acid.

Properties.—Liquor ammonia acetatis is colourless, with a slight smell of acetic acid and ammonia, a feeble saline and somewhat bitter taste, in which that of ammonia is perceptible. This taste of ammonia, which is also perceptible in other salts of this base having a neutral reaction, is caused by the free or feebly combined soda in the saliva combining with the acid and evolving the ammonia. At a gentle heat it must entirely volatilize. It must react either alkaline or neutral, but by no means acid. When exposed for a length of time to the air it undergoes decomposition, ammonia is evolved, and the acetic acid forms various products, amongst others a flocculent vegetation. It should not be kept any considerable time. Of course it is liable to all the contaminations named under the heads of Acetic Acid and Ammonia.

AMMONIUM OXIDATUM CARBONICUM.

Ammoniæ Carbonas.—Sal cornu cervi Volatilis.—Sesquicarbonate of Ammonia.

FORMULA: $2NH_4O + 3CO_2$.

Preparation.—1 Part of sal ammoniac, powdered as finely as possible, is intimately mixed with 1½

part of carbonate of lime (chalk), the mixture is exposed in a sand bath for an hour or two, according to the quantity, to a gentle heat until all the moisture is driven off, and is then quickly transferred to a cast iron retort, having a short wide neck dipping into a large glass receiver, without being luted, and the retort heated so long as ammoniacal fumes are evolved. In order to prevent the receiver from becoming too hot, it is best to pass the neck of the retort through a hole in the side of the furnace made on purpose, and also to cool it with a stream of cold water. In emptying the receiver it is often necessary to break it; and this is best done by just cracking the neck with a stone, then applying a red hot iron to the place, and immediately afterwards a drop or two of cold water. The salt is to be quickly put into well-closed vessels. Failing an iron retort a glass one may be used, but it will be necessary to coat it well with clay to prevent its cracking or melting during the operation. Such a luting may be prepared by dissolving borax in 8 parts of warm water, and adding so much slaked lime that a thick pap is formed, which is painted over the retort three or four times consecutively with a brush. When dry a thin paste of linseed oil and slaked lime is applied the same number of times. If the luting cracks in the fire, more of the last paste is applied to the spot and sprinkled with finely-powdered slaked lime. The yield will be about $\frac{2}{3}$ of the weight of the sal ammoniac employed.

Recapitulation.—If a mixture of sal ammoniac (NH_4Cl) and carbonate of lime ($CaO + CO_2$) is exposed to a high temperature, decomposition ensues; the lime yields its oxygen to the ammonium, the calcium combines with the chlorine, and remains behind as chloride of calcium, whilst the carbonic acid passes to the oxide of ammonium; but only $\frac{1}{3}$ of the latter unite with it, so that a combination

of 2 at. oxide of ammonium and 3 at. carbonic acid pass over, together with oxide of ammonium.

3 at. NH_4Cl, and 3 at. $CaO + CO_2$, form
3 at. CaCl, 1 at. $2NH_4O + 3CO_2$, and 1 at. NH_4O ($NH_3 + HO$).

668 Parts of sal ammoniac do not require more than 625 parts of carbonate of lime, but as the chalk is not pure carbonate of lime and an excess is by no means prejudicial, half as much again is employed. A thorough decomposition ensues only at a low red heat, consequently the employment of an open fire is unavoidable.

If the mixture were not previously well dried, a moist mass is obtained on distillation, instead of a fine dry salt.

The residue may be employed for chloride of calcium.

Properties.—The sesquicarbonate of ammonia is a firm white crystalline crust, smelling strongly of ammonia, and tasting and reacting strongly alkaline, entirely volatile at a gentle heat, soluble in 2 parts of cold water, but not in alcohol. If not carefully excluded from the air, its composition becomes altered, it suffers a considerable loss of weight, and lastly falls into a powder. This change does not consist, as is generally stated, in absorption of carbonic acid from the air, but a separation of the salt into bicarbonate and simple carbonate of ammonia.

1 at. $2NH_4O + 3CO_2$, forms
1 at. $NH_4O + 2CO_2 + HO$, and 1 at. $NH_3 + CO_2$.

Of these two products the last named quickly evaporates, leaving the bicarbonate, which, at the ordinary temperature, is more slowly volatilized. The bicarbonate of ammonia dissolves in 8 parts of cold water; consequently, should the carbonate of ammonia re-

quire more than 2 parts of water for its solution, it contains *bicarbonate*. If a white insoluble residue is left on treating with water, which dissolves with effervescence in nitric acid, and blackens with sulphuretted hydrogen, *lead* is present (carbonate of lead). In many factories leaden receivers are used, and if, when the salt is extracted, any portions of lead adhere to it, they quickly become converted into carbonate, from the action of the salt and the oxygen of the air. If the solution, supersaturated with nitric acid, gives with nitrate of silver a white precipitate, becoming violet on exposure to the light, *chlorine* (from volatilized, undecomposed sal ammoniac) is present. *Iron* is detected if tannic acid causes a violet or blue precipitate of tannate of iron in the solution after it has been carefully neutralized with hydrochloric acid.

From the slightest contact of this salt with copper or brass utensils it instantly acquires a blue colour. In powdering it, therefore, an iron or porcelain mortar must be used.

AMMONIUM OXYDATUM NITRICUM.

Ammoniæ Nitras.—Nitrum Flammans.—Nitrate of Ammonia.

FORMULA: $NH_4O + NO_5$.

Preparation.—Any convenient quantity of pure nitric acid is treated in a porcelain dish, and well stirred, with caustic liquor ammonia, until it no longer reddens litmus paper. To 1 part acid, of spec. grav. 1·41, somewhat more than 2 parts of liquor ammonia, spec. grav. 0·960, are requisite. The liquid is evaporated gently to crystallization. The crystals are well drained, or dried between blotting paper, and the air excluded. 1 Part of acid, 1·41, forms about $\frac{2}{3}$ part of salt.

Recapitulation.—The formation of the salt simply consists in the saturation of the acid with ammonia, and its combination with water of crystallization.

1 at. NO_5, 1 at. NH_3, and 1 at. HO, form
1 at. $NH_4O + NO_5$.

675 Parts of anhydrous, or 1237 parts of acid containing 5 at. of water (the 2nd hydrate, =1·41 spec. grav.) require 213 part of anhydrous, or 2130 parts of ammonia, containing 90 per ct. of water (spec. grav. 0·960). In order to insure entire saturation rather more ammonia is employed, as the excess passes off on evaporation. The crystals must be removed from contact with the air as quickly as possible, otherwise they attract moisture and deliquesce.

Properties.—Nitrate of Ammonia crystallizes in long, colourless, flexible crystals, odourless, and of a sharp, saline, and cooling taste. In the heat they fuse and volatilize, but are during the process entirely decomposed into water and nitrous oxide.

1 at. $NH_4O + NO_5$, forms
2 at. NO, and 4 at. HO.

It attracts moisture from the air, and is readily soluble in alcohol, as well as water; its solution has an acid reaction, like sal ammoniac, but rather more intense. In testing for impurities, those likely to occur in nitric acid or caustic ammonia must be looked for; viz. *sulphuric acid*, *chlorine* (*iodine*), *lime*, and *metals* (*copper*), which may be detected by chloride of barium, nitrate of silver, oxalate of ammonia, and sulphuretted hydrogen.

AMMONIUM OXIDATUM OXALICUM.

Ammoniæ Oxalas.—Oxalate of Ammonia.

FORMULA: $NH_4O + C_2O_3 + HO$.

Preparation.—Any quantity of pure oxalic acid is dissolved in a porcelain dish with twice its weight of distilled water, and the solution supersaturated with liquor ammonia (to 1 part of crystallized acid 3 parts of liquor ammonia), and the whole placed in a cool spot. After 24 hours the crystals are separated from the mother liquor, and the latter reduced by evaporation. The crystals are collected, and spread on filtering paper to dry, without the application of heat. Their weight is somewhat more than that of the acid used.

Recapitulation.—Similar to the nitrate of ammonia. 788 Parts of crystallized oxalic acid require 213 parts of anhydrous or 2130 parts of liquor ammonia.

Properties.—Neutral oxalate of ammonia forms delicate white four-sided prisms, which are odourless and of a penetrating taste. In a warm atmosphere they lose 1 at. of water; heated, they melt and volatilize, entirely decomposing and forming a peculiar white, odourless, and tasteless body $= NH_2 + C_2O_2$.

1 at. $NH_4O + C_2O_3 + HO$ form;
1 at. $NH_2 + C_2O_2$ and 3 at. HO.

It is soluble in 25 parts of cold, more readily in hot water, but insoluble in alcohol. The most probable contaminations are, *sulphuric acid*, *chlorine*, *nitric acid*, indicated by chloride of barium, nitrate of silver, and indigo solution; and lastly, *potash*, which may be detected as giving, after burning in a platina crucible, a strongly alkaline residue.

AMMONIUM OXIDATUM PHOSPHORICUM.

Ammoniæ Phosphas.—Phosphate of Ammonia.

Formula: $2NH_4O + P_2O_5 + HO$.

Preparation.—Pure liquid phosphoric acid is supersaturated in a porcelain dish with liquor ammonia, (1 part of acid spec. grav. 1·160 requires rather more than 1 part of liquor ammonia,) and evaporated to crystallization. The solution must as in the case of nitrate of ammonia, be very much reduced in bulk before it crystallizes. The crystals are spread out on filtering paper to dry. Their weight is about $\frac{1}{3}$ that of the acid employed.

Recapitulation.—As by nitrate of ammonia. 900 Parts of anhydrous or 3912 parts of acid, spec. grav. 1·160 (containing 77 per ct. water) require 4260 parts liquor ammonia.

Properties.—Neutral phosphate of ammonia forms colourless oblique rhombic tabular crystals, odorless and of a cool penetrating taste; when heated they melt, and at a red heat lose their base, phosphoric acid remaining.* In cold water the salt readily dissolves and the solution has a slightly acid reaction. Alcohol does not dissolve it. The impurities may be *sulphuric acid*, *chlorine*, *arsenious acid*, *nitric acid*, and all those mentioned under the head of Phosphoric Acid.

* But still not entirely free from ammonia.—Ed.

AMMONIUM OXIDATUM SUCCINICUM.

Ammoniæ Succinas.—Succinate of Ammonia.

FORMULA: $(NH_4O + C_4H_2O_3) + HO + xAq.$

Preparation.—Pure crystallized succinic acid is finely powdered, and liquor ammonia added to complete saturation. 1 Part of acid requires about 3 parts of ammonia. The neutral solution is the form employed for analytical purposes. The compound may be obtained crystallized, but from loss of ammonia is always an acid salt.

For medicinal purposes the impure succinic acid is neutralized with common carbonate of ammonia, (4 parts of acid require about 5 parts of carbonate of ammonia) and the solution either crystallized, or when diluted with the requisite quantity of water, preserved as liquor ammonii succinici, or liquor cornu cervi succinatus.

Recapitulation.—As by nitrate of ammonia. 742 Parts of crystallized succinic acid are saturated by 2130 parts of hydrated ammonia. When rough acid and common carbonate of ammonia are used, the carbonic acid is evolved, and a great portion of the empyreumatic oily matter present in both, remains undissolved, and may be separated by filtration.

Properties.—The pure neutral solution of succinate of ammonia is colourless, has the odour and taste of ammonia, and yields on evaporation, whilst ammonia is evolved, colourless prismatic crystals of a sharp bitter cooling taste, insoluble in alcohol but dissolving in water and having a powerfully acid reaction. Before using these crystals as a reagent, they must be neutralized with ammonia. Heated, it is entirely volatile. That prepared with the raw acid has the peculiar odour of the empyreumatic oil, a yellowish-brown colour, and leaves on evapo-

ration, a trace of carbon. The other tests of impurities are the same as with succinic acid.

AMMONIUM OXIDATUM SULPHURICUM.

Ammoniæ Sulphas.—Sal Ammoniacus secretus Glauberi.—Sulphate of Ammonia.

FORMULA: $NH_4O + SO_3 + HO$.

Preparation.—Pure sulphuric acid is diluted with its weight of water, then saturated with solution of caustic ammonia (to 1 part of concentrated acid about 3½ parts liquor ammonia) and the liquor allowed to crystallize. The crystals, spread on filtering paper, are dried in the air. They weigh about half as much more as the acid used.

Recapitulation.—As by nitrate of ammonia. 613 Parts of monohydrated sulphuric acid require 213 parts of anhydrous, or 2130 parts of hydrated ammonia for saturation.

Properties.—Sulphate of ammonia forms colourless six-sided prisms, having no odour, but of a pungent bitter saline taste; it dissolves in 2 parts of cold water, less of hot, and is insoluble in alcohol. The solution has a very faint acid reaction. The salt is slightly efflorescent in warm air; heated, it melts, and is entirely volatilized, but decomposes at the same time into sulphurous acid, water, ammonia, and nitrogen; (*Vide* AMMON. CHLORATUM). It may contain chloride of ammonium, and all the impurities of the sulphuric acid.

AMMONIUM SULPHURATUM LIQUIDUM.

Liquor Ammonii Sulphurati.—Hydrosulphate of Ammonia.—Sulphide of Ammonium.

FORMULA: $NH_4 + S + xHO$.

Preparation.—An apparatus similar to that described under ACIDUM HYDROSULPHURICUM is used. In the evolution flask (*a*) are placed 7 parts of dilute sulphuric acid, in the wash bottle (*b*) a few ounces of pure water, in the bottle (*c*) 4 parts of caustic liquor ammonia, spec. grav. 0·960, and lastly when the whole of the apparatus is arranged, 1 part of sulphuret of iron is introduced into the acid. The evolution of the gas is facilitated by a gentle heat, and the bottle (*c*) which is only to be lightly closed is cooled by ice or cold water. When no more gas bubbles are given off, the corks (*d*) and (*e*) are quickly removed to prevent absorption taking place, and the bottle (*c*) carefully closed and set aside for some days when if any black flocculent matter separates, it is filtered off or decanted. It will weigh about $\frac{1}{10}$ more than the liquor ammonia used.

Directions are generally given to pass sulphuretted hydrogen into liquor ammonia until it no longer causes a precipitate with sulphate of magnesia; this point is attained when the ammonia is only half saturated, that is, when the liquid still contains a quantity of free ammonia.

Recapitulation.—The reaction which ensues on the contact of dilute sulphuric acid with sulphate of iron has already been explained under ACID HYDROSULPHURICUM. From the decomposition of the water, protoxide of iron which combines with the sulphuric acid, and sulphuretted hydrogen are formed. The hydrogen of the gas combines with ammonia, forming ammonium, which unites with

the sulphur to sulphide of ammonium, or hydrosulphuret of ammonia

1 at. HS and 1 at. NH_3, form
1 at. $NH_3 + HS$, or 1 at. NH_4S.

As 1 at. HS is evolved from 1 at. sulphuret of iron, so for 550 parts of the latter 2130 parts of liquor ammonia spec. grav. 0·960 are requisite, or 1 part to 4. The bottle containing the ammonia must be well cooled, as the gases in assuming a liquid form evolve a quantity of heat. The gas is washed to separate anything that may have been carried over from the evolution flask; nevertheless, it generally happens either during the process, or, as is more frequently the case, after standing, that a black flocculent matter subsides, this is sulphuret of iron and may be removed by decantation or filtration. It is not very certain in what form the iron passes over, it can scarcely be mechanical, otherwise sulphuric acid should be present, which is not the case, when it has been washed; probably it is in combination with hydrogen, which entering the ammonia with the sulphide of hydrogen then becomes decomposed. This compound of iron and hydrogen occurs when metallic iron is dissolved in dilute sulphuric or hydrochloric acid; and we may here remark that sulphuret of iron generally contains small particles of iron not thoroughly combined with sulphur. So soon as the ferruginated hydrogen comes in contact with sulphide of ammonium they decompose into sulphide of iron, ammonia, and hydrogen.

1 at. FeH and 1 at. NH_4S, form
1 at. FeS, 1 at. NH_3, and 2 at. H.

That the ferruginated hydrogen, or ferride of hydrogen, has the formula FeH has never been demonstrated by experiment, and I have merely

judged so from analogy. I have not mentioned it under the article ACID HYDRO-SULPHURICUM, as its presence is not perceptible, for, in the first place, ferruginated hydrogen and sulphide of hydrogen may remain in contact without disturbing their respective elements; and secondly, on decomposing a good sulphide of iron this gas is given off in so slight a degree that its presence is scarcely appreciable in solution of sulphide of hydrogen.

Properties.—Freshly prepared liquid sulphide of ammonium is colourless, of an hepatic and ammoniacal odour and taste. It fumes in the air, becoming decomposed through the action of the aqueous vapours, into sulphuretted hydrogen and liquor ammonia, both known by their peculiar odours. From the action of the oxygen of the air, the sulphuretted hydrogen is decomposed, forming water with separation of sulphur, which, being dissolved by the undecomposed hydrosulphuret of ammonia, the latter acquires a yellow colour. (A small portion of sulphur is however lost, being dissipated in extremely fine particles with the ammonia and watery vapours, giving them the appearance of a white smoke). For this reason, this preparation soon acquires a yellow colour, if the bottle is frequently opened. And if not carefully guarded against, this decomposition may go on until all the sulphur is precipitated, and the reagent become useless.

AMYGDALINUM.

Amygdaline.

FORMULA $C_{40}H_{27}O_{22}N$.

Preparation.—Bitter almonds are coarsely powdered, warmed with constant stirring in an iron pot, until on squeezing between the fingers they give

out oil, are packed in warmed horse-hair bags, between the warm plates of a screw, or, still better, an hydraulic press, and strongly expressed. When all the oil has run off, the cake is powdered as finely as possible, and the powder digested for six hours in a tinned copper still, with three times its weight of alcohol, 80 per ct. (spec. grav. 0·840), at such a temperature that the latter continually boils very gently. As soon as the still is sufficiently cool to bear the hand on it, the contents are emptied into a thick linen bag, the retort rinsed out with the alcohol that has distilled over, the bag is pressed, and the residual mass digested again with a similar quantity of alcohol as at first, and expressed. The still is then well cleaned, the two quantities of expressed liquors are replaced in it, and very gently warmed for an hour, then carefully poured from the fatty oil that has subsided and filtered. Besides the fatty oil, a little amygdaline will generally be deposited, this may be separated from the former by filtration and expression between filtering paper. When freed as much as possible from oil, the amygdaline is added to the filtered spirituous solutions, and the latter reduced by distillation to one-sixth, the residue is then filtered through paper moistened with water, and evaporated in a porcelain dish, at a very moderate temperature, to the consistence of a thin syrup; then placed for several days in a cool place. When the syrup has solidified to a crystalline mass, it is mixed with half its volume of alcohol of 80 per ct., placed on a filter, and washed with a little cold alcohol, the pasty mass is poured into a glass flask with about twice its volume of alcohol of 80 per ct., heated to boiling, filtered, if necessary, whilst hot, and allowed to crystallize. The mother liquor will yield more crystals on evaporation. The crystals are spread on filtering paper, dried in the air, and finally in a water bath. It is now quite pure enough for medicinal purposes,

but contains traces of fatty oil, which are only to be removed by repeatedly treating with ether. The yield will be from 1 to 2 per ct.

Recapitulation.—Amygdaline exists in the bitter almonds uncombined; it cannot, however, be extracted with water, as the latter dissolves emulsin also (a peculiar albuminous substance) which, reacting on the amygdaline, decomposes it; (*Vide* end of this article). The alcohol on the other hand, dissolves the amygdaline, but not the emulsin. By expressing previous to the extraction with alcohol most of the fatty oil is removed, which would otherwise interfere with the purification of the amygdaline. The almonds and press must not be heated beyond the temperature of boiling water, otherwise a little amygdaline is decomposed. The mass after its digestion is strained whilst warm, otherwise a portion of the amygdaline which deposits on cooling would be lost. In order the more readily to separate the expressed fatty oil from the spirituous solution, the latter is again gently warmed. The purification of the crystalline mass with cold alcohol is due to the slight solubility of the amygdaline in this menstruum, and the readiness with which the accompanying extractive and saccharine matter dissolve in it. By recrystallizing, the remainder of the fatty oil is mostly removed. When dried in a water bath, some water chemically combined is removed. It crystallizes, according to Liebig and Wöhler, out of a saturated alcoholic solution, at 104° Fah., in colourless transparent prisms containing 6 at. of water, but it loses these at 212° Fah. The treatment with ether removes the last traces of fatty oil from the amygdaline which is insoluble in this menstruum.

The expressed oil is about $\frac{1}{3}$ the weight of the almonds, and may be applied to the same purposes as that from sweet almonds.

Properties —Pure Amygdaline forms white anhy-

drous soft mother-of-pearl, like glittering scales, which heated in a platina spoon give no residue; they are odourless, slightly bitter, readily soluble in water and hot alcohol, but with difficulty in cold. If the watery solution be milky or opalescent a little fatty oil still adheres to the amygdaline, which, in consequence of the necessary application of heat during the preparation has become rancid; the last traces of oil are,however only to be removed by ether, (in which the amygdaline is insoluble), and, for this reason, when it has not been treated with ether, it possesses a rancid oily smell. The best test for amygdaline, is the behaviour of its watery solution with emulsin, a peculiar albuminous matter found both in the bitter and sweet almond, which converts it into 1 at. prussic acid = HCy, 2 at. of hydruret of benzoyle or bitter almond oil = $2C_{14}H_6O_2$ (which together form the ethereal oil containing prussic acid which bitter almonds yield on distillation with water) $\frac{1}{2}$ an at. grape sugar = $C_6H_7O_7 = C_6H_6O_6 + HO$, 2 at. formic acid = 2 C_2HO_3 and 5 at. water = 5 HO;

	C.	H.	O.	N.
1 at. Prussic Acid	2	1	—	1
2 at. Hydruret of Benzoyle .	28	12	4	—
$\frac{1}{2}$ at. Grape Sugar	6	7	7	—
2 at. Formic Acid	4	2	6	—
5 at. Water	—	5	5	—
	C_{40}	H_{27}	O_{22}	N_1

In this case the emulsin appears to act as a ferment but the exact manner of its action is unknown. Prussic acid does not exist in the almonds but is first evolved or produced by the action of the water, which dissolves the emulsin and amygdaline and allows them to react on each other. Consequently, if an emulsion of sweet almonds is mixed with amygdaline, the odour of prussic acid is instantly

given off, and 17 grains of amygdaline form 1 grain of anhydrous prussic acid; for the atom of amygdaline = 5713 divided by the atomic weight of prussic acid = 337, gives 17 as a quotient.

AMYLUM IODATUM.

Amyli Iodidum.—Iodide of Starch.

FORMULA: $C_{12}H_{10}O_{10} + xI$.

Preparation.—24 Parts of starch powder are rubbed with 24 parts of cold distilled water to a paste, to this a solution of 1 part of iodine in 12 parts of alcohol is added, and when well mixed the whole is thrown on a filter and washed with cold distilled water until the liquid runs off perfectly colourless. The contents of the filter are now dried between bibulous paper without heat, and preserved in a well-closed bottle.

Recapitulation.—Starch powder is quite insoluble in cold water, but, when mixed with it, combines with iodine to an equally insoluble compound of a bluish black colour. The above mentioned quantity of iodine will be almost entirely taken up, any excess however is removed by the cold water.*

Properties.—Iodide of starch is a blueish black powder, odourless, of raw taste like starch powder, and afterwards slightly like iodine. It mixes with water like starch powder, without dissolving; when heated to boiling it does not form a paste, but a slimy mass which at the same time gives off a slight odour of iodine, whilst traces only of the compound are soluble.

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* According to M. Lahens Thoulouse, in the "Journal de Pharmacie," April, 1851, when 9 parts of iodine are heated in a closed vessel for some hours, with one part of starch, at the temperature of boiling water, a soluble compound is obtained.

ARGENTUM OXIDATUM ACETICUM.

Argenti Acetas.—Acetate of Silver.

FORMULA: $AgO + C_4H_3O_3 = AgO + \bar{A}$.

Preparation.—3 Parts of pure nitrate of silver are dissolved in 9 parts of distilled water, and with this is mixed a solution of 2 parts of pure acetate of potash in 9 parts of distilled water; the white curdy mass that is formed is guarded as much as possible from the light and placed in a funnel, the tube of which is loosely closed with a glass stopper; it is then washed with 50 parts of distilled water, allowed to drain, thinly spread on a porcelain plate and dried at the ordinary temperature, light being carefully excluded. The preparation will weigh about 2 parts.

3 Parts of crystallized acetate of soda may be substituted for the acetate of potash.

Recapitulation. — When nitrate of silver and acetate of potash come into contact, an exchange of acids ensues, difficultly-soluble acetate of silver and the readily-soluble nitrate of potash being formed.

1 at. $AgO + NO_5$, and 1 at. $KO + \bar{A}$, form
1 at. $AgO + \bar{A}$, and 1 at. $KO + NO_5$.

2125 Parts of nitrate of silver require 1228 parts of acetate of potash; but it is better to use a small excess of the latter, to ensure entire precipitation. The excess of acetate of potash, together with the nitrate formed, are removed by washing; but this must not be too long continued, as a small portion of the acetate of silver is at the same time dissolved; and it is on this account that the product, which theoretically should nearly equal the weight of nitrate of silver used, is somewhat smaller. In washing it a paper filter must not be used, as the

portion of the salt with which it comes in contact becomes gray, the acetic acid being given off, and the liberated oxide separating into oxygen and metallic silver; and for this same reason the daylight is excluded, and a temperature higher than that of the atmosphere avoided in drying.

The air, which is seldom quite free from sulphuretted hydrogen, may possibly impart to the salt a gray colour, from the formation of sulphuret of silver.

The process is exactly the same with acetate of soda. 2125 Parts of nitrate of silver require 1703 parts of crystallized acetate of soda, $=NaO + \bar{A} + 6Aq$.

The acetate of silver which remains dissolved is precipitated with chloride of sodium, and the precipitate reduced to the metallic state.

Properties.—Acetate of silver is a white crystalline powder, having a feeble odour of acetic acid, and an exceedingly nauseous metallic taste. At ordinary temperatures it dissolves in 100 parts of water, but requires less hot water. A hot saturated solution yields, on cooling, white, soft, mother-of-pearl-like needles. It is slightly taken up by alcohol; its solutions have a neutral reaction. Exposed to the light it acquires a violet-gray colour (*vide supra*), leaving on solution a grayish residue, soluble in nitric acid. Heated it melts, giving off acetic acid, and from the decomposition of a portion of the latter, is blackened, and the silver becomes reduced through the agency of the carbon. If the acetate used in its preparation was not free from *sulphates* or *chlorides*, sulphate or chloride of silver will be present. In the first case its aqueous solution gives, with nitrate of baryta, a precipitate of sulphate of baryta, insoluble in nitric acid. In the second it is not entirely soluble in hot water, and the residue, which becomes violet-coloured in the light, will dissolve in ammonia but not in nitric

acid. When it is not sufficiently washed, *nitrate of potash* will be present, and, on precipitating the silver with hydrochloric acid, filtering, and evaporating the filtrate to dryness, may be detected as a saline residue.

ARGENTUM OXIDATUM NITRICUM.

Argenti Nitras.—Lapis Infernalis.—Lunar Caustic.—Nitrate of Silver.

FORMULA: $AgO + NO_5$.

Two parts of pure silver, in small pieces, are to be dissolved in 3 parts of pure nitric acid, spec. grav. 1·41, diluted with 1½ parts water, at a gentle sand heat,* and the clear solution—after decanting, and filtering the last portions, if necessary—evaporated in a porcelain dish, at first over an open fire, and afterwards, when it has become thick, under constant stirring with a glass rod, to perfect dryness in a sand bath. On account of the nitric acid vapours that are evolved, this process should be performed under a chimney with a good draught.

If the crystallized salt is required, the dried mass is again dissolved in its weight of distilled water, and allowed slowly to evaporate in a sand bath to about half; it is then placed for some days in a cool spot, the mother liquors poured from the separated crystals, and again slowly evaporated. The crystals are not dried on paper, but drained in the vessel in which they formed, dried, and kept in a bottle excluded from the light.

If silver reduced from the chloride be made use of, it should be borne in mind that 4 parts of the latter yield 3 parts of metallic silver, which, being in a very fine state of division, must, in order to prevent too powerful an action, be added in very small portions and gradually.

When required in sticks, a portion (from one to several ounces, according to the size of the mould) is fused over a spirit lamp, in a porcelain dish, being constantly stirred with a glass rod, and the liquid mass poured into a bright iron mould that has been previously warmed. The sticks, as soon as cold, are removed, and the tubes wiped with dry filtering paper, to remove any adhering salt. 8 Parts of pure silver yield 12 parts of nitrate.

The so-called cupelled silver, which always contains a small quantity of copper and generally a trace of gold, serves admirably for the formation of this preparation, if the first crystals that separate are washed with a little cold water, and the mother liquor, which contains all the copper, set aside for purification by reduction. From the above-mentioned silver, the gold generally separates in the form of blackish flakes. Other kinds of silver—as coins and vessels, which contain a good deal of copper—must always be subjected to a purification, otherwise the salt will be contaminated with copper. The continued fusion of nitrate of silver, to remove any copper that may be present, seldom gives perfect results, and causes a loss of silver, from reduction.

Recapitulation.—When silver is brought in contact with moderately-dilute nitric acid, a lively action ensues, even in the cold, yellow fumes are given off, and as the temperature rises the metal is rapidly and entirely dissolved. Before it can combine with the acid, the metal is converted into oxide, and this takes place at the expense of one portion of the acid, which separating into nitric oxide and oxygen, oxidizes three atoms of silver; the nitric oxide as it is given off abstracting 2 at. of oxygen from the air becomes hyponitric acid.

3 at. Ag, and 4 at. NO_5, form
3 at. $AgO + NO_5$, and 1 at. NO_2,

the latter with 2 at. O forming NO_4.

Nitric acid spec. grav. 1·41 contains 54 per ct. of anhydrous acid; 4050 parts of silver require 2700 parts of anhydrous acid, which is contained in 5000 parts of 54 per ct.; rather more acid than this must be taken, to allow for a portion which evaporates during the solution of the metal. The liquid is allowed to deposit,* and the clear portion evaporated to dryness to insure the absence of any free acid, then dissolved in water and crystallized.

All organic matter must, from this as well as all other silver salts, be carefully excluded, as they facilitate their reduction and discolouration, consequently the crystals must not be dried on filtering paper. To fuse the salt, a porcelain dish is most convenient; it is sometimes recommended to rub the surface of the mould with oil, but this is unnecessary and unadvisable, as the sticks slide equally well out of the dry and polished cylinders, and the oil will cause the gray appearance on their outer surface. The salt must be poured into the mould so soon as it is liquefied, as it soon begins to evolve nitric acid, and the oxide formed becomes reduced to a gray metallic covering which is prejudicial to the appearance of the preparation. If such a pellicle has formed (it will mostly remain in the dish after pouring out the fluid portion), a few drops of pure nitric acid must be added to the next portion of the salt, previously to fusing it.

The process of purifying silver from copper, which has often been recommended, by retaining the mixed nitrate in a state of fusion, is based on the greater stability of the nitrate of silver; yellowish-

* The black residue from silver reduced by charcoal is dried and reserved for another reduction, as it generally contains a little chloride of silver.

brown vapours are given off as the freed nitric acid for want of water separates into hyponitric acid = NO_4 and oxygen O. But at the same time the silver salt undergoes a partial but similar decomposition, which will be greater in proportion to the increased contents of copper, on account of the longer fusion to which it must be subjected. If, when the process is finished, the salt be dissolved in water, we certainly obtain a silver solution free from copper, but the black residue is oxide of copper containing silver. The use of an iron spoon for fusing is still less to be recommended, as it causes a quicker decomposition of the silver salt, and the spoon becomes internally coated with a thick crust of metallic silver.

Properties.—Pure nitrate of silver crystallizes in colourless 4 and 6 sided tables, which do not attract moisture from the air, are odourless, and of a bitter sharp metallic taste. It is soluble in its own weight of cold water, more readily in hot water and alcohol; the solution should have no action on litmus paper. The lunar caustic differs from the crystallized only in form, is quite white, and exhibits, when broken, a stellated radiating fracture. Both, when exposed to the light, become gradually gray, in the sunlight instantly, and for the same reason as the Argentum Aceticum. By a continued fusion the salt undergoes entire decomposition, the nitric acid is given off (and evolved as yellowish-brown vapours, being for want of water decomposed into NO_1 and O), together with the oxygen of the oxide of silver, the pure metal remaining. If the lunar caustic has a gray silvery colour, the heat has been continued too long, and caused reduction to take place. If it has a yellow tint, it is due to *oxide of iron*, either from the silver containing this metal, or the mould not being polished. By solution the oxide of iron remains behind. A greenish colour denotes *nitrate of copper*, and such a salt treated

with ammonia yields a dark blue liquid from the formation of ammonio-nitrate of copper. A black colour is caused by the admixture of oxide of copper which has lost its acid in the fusion, and being insoluble in water remains behind. The lunar caustic is adulterated with many substances which are colourless, will fuse, and bear casting with it. Of these, the *nitrate of potash* is readily distinguished by precipitating all the silver as chloride, evaporating to dryness, when the saltpetre will be found in the residue. The *nitrate of lead* may be determined in a similar manner, or more directly by diluting the solution of lunar caustic considerably, and testing with sulphate of soda. Once also I found *nitrate of soda* in the sticks, this causes the latter to attract moisture from the air, and may otherwise be determined like the nitrate of potash. If, after precipitating with hydrochloric acid, evaporating to dryness, and dissolving the residue in water, oxalate of ammonia causes a turbidity, *lime* is present. *Chloride of silver*, which is often present in the commercial salt, remains behind on treatment with water, and is readily taken up by ammonia.

ARGENTUM OXIDATUM SULPHURICUM.

Argenti Sulphas.—Sulphate of Silver.

FORMULA: $AgO + SO_3$.

Preparation.—3 Parts of pure nitrate of silver are dissolved in 9 parts of distilled water, and to this a solution of 3 parts of pure crystallized sulphate of soda in 12 parts of distilled water are added, proceeding as directed under ARGENT. ACET., the product will be rather more than 2 parts.

Recapitulation.—As by ARGENT. ACET.; sulphate of silver and nitrate of soda are formed,

1 at. $AgO + NO_5$, and 1 at. $NaO + SO_3 +$ 10HO, form
1 at. $AgO + SO_3$, 1 at. $NaO + NO_5$, and 10 at. HO.

2125 Parts of nitrate of silver require 2015 parts or nearly as much Glauber's salts.

The sulphate of silver that dissolves in the wash water may be precipitated by hydrochloric acid and reduced to pure silver.

Properties.—Sulphate of silver forms a white crystalline odourless powder, of a metallic taste. 200 Parts of water of the ordinary temperature dissolve 1 part of this salt, the solution having a neutral reaction. Of boiling water it requires scarcely 100 parts, and crystallizes in rhombic pyramids on cooling. It is quite insoluble in alcohol. Exposed to the light it is gradually decomposed, and acquires a gray colour. In the heat it fuses and decomposes, oxygen and sulphuric acid are evolved, metallic silver forming the residue. The method of testing for chloride of silver and nitrate of soda is similar to that under ARGENT. ACET.

ASPARAGINUM.

Althacinum.—Asparagin.—Asparamid.—Althein.

FORMULA: $C_8H_8N_2O_6 + 2HO$.

Preparation.—From Marshmallow Roots.—A portion of this root is sliced, and macerated for 2 days in an earthen dish with four times its weight of cold distilled water, the slimy liquid is strained through a pointed bag, the residue again treated with cold water, strained, and strongly pressed. The liquid, after depositing, is evaporated to half in a copper vessel, allowed to deposit, then strained, and evaporated at a gentle heat in a water bath to the consis-

tence of thick syrup. The extract, which will equal in weight about one-third that of the root, after standing several weeks in the cold, becomes covered with a thick saline crust, which when separated from the fluid is washed with some cold water, and purified by dissolving in three times its weight of hot water, filtering and crystallizing. The remainder of the extract is again put in a cool place, when, after several weeks, a small crust will again form, which may be treated as the first. 130 Parts of root yield about 1 part asparagin.

The root must not be extracted by warm or boiling water, as in this case an infusion is obtained, which evaporated to the weight of the root forms a thick gelatinous mass, from which nothing will crystallize. When this mass is treated with $\frac{3}{4}$ its weight of alcohol of 80 per ct. the mucilage separates and may be strained off; but after distilling the alcohol and evaporating to a syrup, the extract yields, even on standing for a considerable time, but a small quantity of asparagin.

Recapitulation.—Asparagin exists in the roots of the marshmallow ready formed, and in an uncombined state; and the aim in the previously described process is simply to separate as much as possible. If the root be exhausted with heat, the asparagin is transformed into a new substance, aspartate of ammonia, which has the atomic composition of asparagin, minus 2 eq. of water; in other words, the elements of anhydrous asparagin.

1 at. $C_8H_8N_2O_6 + 2HO$, forms
1 at. $NH_3 + C_8H_5NO_6$ and 2 at. HO.

This metamorphosis is due in all probability to the starch in the root, which combining with some of the liberated water is converted into sugar; but whether it forms cane sugar,

1 at. $C_{12}H_{10}O_{10}$ (Starch), and 1 at. HO, form
1 at. $C_{12}H_{11}O_{11}$,

or grape sugar,

1 at. $C_{12}H_{10}O_{10}$, and 4 at. HO, form
1 at. $C_{12}H_{14}O_{14}$,

I must leave undecided. The sugar which analysis has detected in the marshmallow root is not all due to the action of the starch on asparagin, but a portion of it exists ready formed. Cold water will not dissolve starch, and consequently its decomposing effects are avoided.

Properties.—Pure asparagin forms hard, colourless right rhombic prisms, odourless, of a cooling taste, soluble in 4 parts of boiling and 40 parts of moderately cold water, also in hydrated but not in pure alcohol or ether. At a little above the boiling point of water it gives off its water of crystallization; at a higher temperature it melts with evolution of ammonia, froths up, becomes black and burns, leaving a shining black ash, which must be entirely combustible.

BARIUM CHLORATUM.

Barii Chloridum.—Baryta Muriatica.—Terra Ponderosa Salita.—Chloride of Barium.—Muriate of Baryta.

FORMULA: $BaCl + 2HO$.

Preparation.—5 Parts of heavy spar and $1\frac{1}{3}$ of wood charcoal, both being finely powdered, are intimately mixed, pressed into an earthen or blacklead crucible, and a thin layer of charcoal laid on the surface; the crucible is covered with a lid fastened on by iron wire, then luted almost entirely with clay, and when this is dry placed on a piece of tile in a good wind furnace; at first a gentle heat is applied, and when the crucible is thoroughly warmed this is increased to a white heat, and continued for

from 1—3 hours according to the quantity of the mixture. To insure entire decomposition the crucible should not contain more than 100 ounces at once. When cold the contents are well stirred with 15 parts of distilled or rain water in an earthen vessel that will hold at least 30 parts, the latter placed in the open air, and common hydrochloric acid added gradually in small portions so long as it causes a strong effervescence, and until the solution only feebly browns turmeric paper. It is not possible to state the exact quantity of hydrochloric acid requisite, as the sulphate of baryta is seldom entirely decomposed into sulphuret of barium by the charcoal; as a general rule 4 parts of acid spec. grav. 1·130 will suffice. On account of the sulphuretted hydrogen care must be taken not to inhale any of the gas evolved. The solution is now filtered, and mixed with sufficient hydrochloric acid to destroy the alkaline secretion, then evaporated until tabular crystals form. The yield should at least equal the quantity of heavy spar employed, though for the reason previously given it seldom exceeds 4 parts.

Recapitulation. — Heavy spar is a sulphate of baryta, as formed in its natural state generally contaminated with copper, iron, manganese, magnesia, lime and strontian; when heated with charcoal to strong redness it yields up its oxygen and forms with excess of carbon carbonic oxide, which is evolved, and sulphuret of barium remaining behind.

1 at. $BaO + SO_3$, and 4 at. C, form
1 at. BaS and 4 at. CO.

1456 Parts of heavy spar require 300 parts of pure carbon, but on account of the impurities of wood charcoal an excess is allowed, or $1\frac{1}{2}$ of charcoal to 5 of heavy spar. The sulphates of other metals present also become converted by the charcoal into sulphurets. The layer of powdered charcoal spread on the surface prevents the oxidizing action of the air.

Whilst being mixed with water the mass must be well stirred, otherwise lumps as hard as stone form, which resist for some time even the action of the acid. The acid when added forms sulphuretted hydrogen and chloride of barium.

1 at. BaS, and 1 at. ClH, form
1 at. BaCl and 1 at. HS,

the greater part of the latter being given off with effervescence; and on this account a large dish is necessary, whilst from the poisonous nature of the gas the operation must be performed in the open air. The sulphuret of barium must not be thoroughly decomposed at first, to prevent the solution of the sulphurets of iron, copper, and manganese, which may now be separated by filtration; after this the remainder of the sulphuret of barium is converted by an excess of hydrochloric acid into chloride of barium. From the crystals obtained on evaporation only such as have a tabular form may be regarded as pure chloride of barium; the latter portions formed, which contain needle-shaped crystals or do not become dry in the air, are either treated with strong alcohol (which dissolves the impurities, leaving the pure chloride of barium), or else retained for particular purposes, as the detection of sulphates in analysis, &c.

On treating the heated mass with hydrochloric acid, the heavy spar that has not been reduced to sulphuret separates; this is collected and reserved for a future operation.

Properties.—Chloride of barium forms transparent right rhombic tabular crystals generally flattened at the corners, odourless, of a disagreeable sharp taste, permanent in the air; it is soluble in $2\frac{1}{2}$ parts of cold and $1\frac{1}{2}$ of boiling water, and insoluble in strong alcohol; heated it loses its water of crystallization, and at a higher temperature fuses to a clear liquid. If the salt attracts moisture from the air it contains

chloride of calcium; this is proved by shaking the finely powdered salt with absolute alcohol, which dissolves any chloride of calcium or strontium present, filtering, evaporating the filtrate, treating the residue with water and then with dilute sulphuric acid; a precipitate denotes *strontium*, this is filtered off, and after saturating the filtrate with ammonia oxalate of ammonia is added, and any turbidity caused by it is due to *lime*. The solution of chloride of barium must be so thoroughly precipitated by sulphuric acid as to yield on evaporation no residue; should there be a permanent one on heating, it is due to impurities. A blue precipitate with ferrocyanide of potassium denotes *iron* (*vide* ACIDUM ACETICUM); with ammonia a white precipitate disappearing on the addition of sal ammoniac from *magnesia*, the chloride of which like that of calcium deliquesces in the air, and may also be a cause of the moisture of the chloride of barium. A blue colour caused by the ammonia arises from *copper*.

BARIUM OXIDATUM PURUM.

Baryta Pura.—Caustic Baryta.—Oxide of Barium.—Pure Baryta.

FORMULA: $BaO + HO + 8Aq$.

Preparation.—(a) From Sulphuret of Barium with Oxide of Copper.— Sulphate of baryta is converted into sulphuret of barium, as described in the previous article, and treated in a porcelain dish with eight times its weight of pure water; heated to boiling whilst constantly stirring, and copper scales added, (those made by the coppersmith when hammering heated copper,) until a small portion when tested gives a pale blue precipitate with sulphate of copper solution, instead of a black or brown one. For 5 parts of heavy spar about 2 parts of copper

scales will be necessary. The fluid portion is now filtered from the black residue into a glass cylinder, the contents of the filter washed with a little hot water, the cylinder tied over with bladder and put in a cool place for 24 hours. The crystals which separate are dried as quickly as possible between filtering paper, and kept in a well-closed bottle. The mother liquor is either kept and used as aqua baryta, or when required in the solid state still further evaporated; and in order to exclude the air this evaporation should be conducted in a retort, in which it may be allowed to crystallize. 5 Parts of sulphate of baryta form from 4 to 5 parts of crystallized caustic baryta.

If copper hammer scales are not obtainable and pure oxide of copper is too expensive for the purpose, the following method, a very good one, may be followed.

(*b*) *From Nitrate of Baryta with Metallic Iron.*—8 Parts of nitrate of baryta are finely powdered and mixed with 3 parts of iron filings; the mixture is thrown, by a spoonful at a time, into a red hot crucible. When the mass ceases to froth up, and becomes pasty and crumbling, it is removed with an iron spatula and powdered as soon as cool. The crucible (to which some portion still adheres) is now boiled with 64 parts of water for half an hour, then removed, the powdered mass mixed with the boiling liquid, 16 parts more water are added, and the whole boiled for another half hour, filtered into a closed vessel, allowed to stand quietly for one day, and proceeded with as that from the process (*a*). About 5 parts of crystallized baryta will be obtained.

By heating the nitrate of baryta alone a disproportionably long time is required, and I have not been able to remove all the nitric acid from 8 ounces of salt by heating to redness for two days. Carbonate of baryta is only partially reduced to the caustic state by charcoal in an ordinary furnace.

Recapitulation.—(*a*) When a solution of sulphuret of barium (*vide* BARIUM CHLORATUM) is mixed with copper scales, (a mixture of protoxide with a little peroxide and metallic copper,) the oxygen of the scales passes over to the barium, forming baryta, and the copper combines with the sulphur to insoluble sulphuret of copper, separable from the solution by filtration. If the scales were pure protoxide,

1 at. BaS, and 1 at. Cu_2O, would form
1 at. BaO and 1 at. Cu_2S,

or 1056 Parts of sulphuret of barium would require 802 parts of protoxide, or for $3\frac{3}{4}$ of sulphuret of barium (obtained by entirely decomposing 5 parts of heavy spar), $3\frac{3}{10}$ of protoxide of copper. Less than this is really necessary, as the scales also contain oxide of copper. The oxide forms sulphuret of copper.

1 at. BaS, and 1 at. CuO, form
1 at. BaO and 1 at. CuS.

The metallic copper like the suboxide is converted into subsulphuret, but at the same time water is decomposed and hydrogen gas given off.

1 at. BaS, 2 at. Cu, and 1 at. HO, form
1 at. BaO, 1 at. Cu_2S, and 1 at. H.

With the boiling, filtering, evaporation, &c., it is necessary to proceed quickly, and thus so far as possible exclude the air, otherwise the baryta will abstract the carbonic acid (for which it has a great affinity) from the atmosphere and become insoluble. This unavoidable evil, as well as the fact that by heating the heavy spar with charcoal a small portion of it escapes reduction, accounts for the yield of caustic baryta, which from 5 parts of heavy spar should equal 7, but always is far below it.

(*b*) The nitrate of baryta gives off its acid at a red heat, which for want of water is decomposed into

oxygen and brownish-yellow vapours of hyponitric acid = NO_4. The decomposition of the salt proceeds but slowly; when however it is in contact with a body having a strong affinity for oxygen, as iron, it decomposes rapidly: the latter abstracts from the nitric acid 3 at. of oxygen, being converted into oxide, whilst nitric oxide is evolved (which coming in contact with the air forms NO_4).

1 at. $BaO + NO_5$, and 2 at. Fe, form
1 at. BaO, 1 at. Fe_2O_3, and 1 at. NO_2.

1631 Parts of nitrate of baryta require 700 parts of metallic iron, or 8 parts nearly 3 parts. If the directions have been carefully followed, the contents of the crucible will be free from a trace of nitrogen, as treatment with sulphuric acid and a drop of solution of indigo will prove. The rest of the manipulation requires no explanation. The yield of crystallized baryta is less than denoted by theory, as 8 parts of nitrate should really produce 10 parts. This is occasioned both by the action of the carbonic acid of the air, and also that a portion of the baryta combines with the oxide of iron to an insoluble compound. It is nevertheless far preferable to heat the nitrate of baryta with iron than alone.

Properties.—Caustic baryta crystallizes from its aqueous solution in transparent tabular and prismatic crystals, having an intense alkaline taste, and acquiring in the air, from the action of carbonic acid, a white covering. Heated, it loses 8 at. of water (45½ per ct.). The last atom, however, is not driven off at any temperature. The crystals are soluble in 19 parts of water of the ordinary temperature, and in 2 parts of boiling water; the solution tastes and reacts strongly alkaline, and acquires in the air a white coating of carbonate of baryta. Caustic baryta is also soluble in spirit, but much less so than in water. To detect *Strontian*, saturate with dilute hydrochloric acid, evaporate

to dryness, agitate the residue with alcohol, and inflame the latter; it should be stirred with a glass rod, and strontian will impart a red colour to the flame. Nitrate of strontian is soluble in alcohol, and imparts to it a red colour on combustion, neither of which properties belong to chloride of barium. *Lime*, after throwing down baryta and strontian, with sulphuric acid, is readily detected in the supernatant liquid on mixing it with alcohol, which will entirely precipitate the sulphate of lime.

BARIUM OXIDATUM ACETICUM.

Barytæ Acetas.—Baryta Acetica.—Acetate of Baryta.

Formula: $BaO + C_4H_3O_3 + HO$.

Preparation.—As this salt is not largely used, it is best made from the pure carbonate of baryta. Concentrated acetic acid is diluted with its weight of distilled water, the mixture gently warmed in a porcelain dish, and carbonate of baryta gradually added, so long as it is dissolved (3 parts of acid spec. grav. 1·045 dissolve about 2 parts of carbonate of baryta), filtered, and the clear liquid allowed slowly to evaporate. The crystals which form are dried on filtering paper in the air, and kept in a closed bottle. 3 Parts of carbonate give 4 of Acetate baryta.

Recapitulation.—Acetic acid drives out the carbonic acid, combining with the baryta to form a readily soluble salt. The acid is first diluted to facilitate the filtration from the excess of carbonate of baryta. As the salt is nearly as soluble in cold as in hot water, it is not obtained in crystals by cooling the hot solution.

Properties.—Acetate of baryta forms colourless rhombic prisms, of a feeble acetic acid smell, pun-

gent bitter taste, and becoming white in the air from loss of water. 100 Parts of cold water dissolve 80, 100 of boiling water 90 parts of the salt; the solution has a neutral reaction, and gradually becomes decomposed, carbonate of baryta and a flocculent body being precipitated. The salt is slightly soluble in alcohol. The test for lime and strontian are the same as with caustic baryta.

BARIUM OXIDATUM CHLORICUM.

Barytæ Chloras.—Baryta Chlorica.—Chlorate of Baryta.

FORMULA: $BaO + ClO_5 + HO$.

Preparation.—3 Parts of crystallized sulphate of ammonia, and 5 parts of chlorate of potash, are dissolved together in a porcelain dish in 15 parts of hot water, the solution constantly stirred, evaporated in a water bath to a thin pasty consistence, and when cold placed in a capacious glass flask, and treated with four times its weight of alcohol of 80 per ct., digested with it for one day at a moderate temperature, then filtered, and the residue well washed with alcohol. The mixed alcoholic solutions are treated with a fourth of their weight of water, the alcohol distilled off, the solution poured into a porcelain dish, the latter placed on a water bath, and, whilst constantly stirring, a freshly-prepared and concentrated hot solution of caustic baryta is added so long as any ammonia is given off, and until the liquid has an alkaline reaction; it is then evaporated to dryness. The dried salt is dissolved in five times its weight of water, and if the solution has an alkaline reaction a stream of carbonic acid is passed through it, the white precipitate is filtered off, and the liquid evaporated to crystalliza-

tion. The crystals are dried on filtering paper, at a moderate temperature. Their weight should be somewhat over 6 parts.

The method just described is exactly similar to that employed in the preparation of chlorate of soda, and one that I have always found most to be depended on. If we pass chlorine into a solution of caustic baryta (from its total insolubility carbonate of baryta is inapplicable), chloride of barium is formed at the same time, and in greater quantity than chlorate of baryta; and from their possessing nearly the same solubility in water, the two salts are not separable by crystallization. Alcohol is also useless in this case, as the chlorate of baryta is only slightly, and the chloride of barium not at all soluble in the menstruum. Chlorate of baryta is not more readily obtained by treating with chlorine a mixture of 1 at. of chloride of barium, and 6 at. of lime, as directed for chlorate of potash (*vide* NATRUM, OXIDUM CHLORICUM). The method of throwing down the potash with hydrofluosilicic acid from chlorate of potash, and then saturating with baryta, is more expensive than the one we have first described, and gives a product contaminated with potash.

Recapitulation.—When sulphate of ammonia and chlorate of potash come together in aqueous solution they exchange elements, forming two salts, also soluble, chlorate of ammonia, and sulphate of potash.

1 at. $NH_4O + SO_3 + HO$, and 1 at. $KO + ClO_5$, form 1 at. $NH_4O + ClO_5$, 1 at. $KO + SO_3$ and 1 at. HO.

938 Parts of crystallized sulphate of ammonia require 1533 parts of chlorate of potash. The two newly-formed salts are separable by alcohol, in which sulphate of potash is insoluble, when the greater portion of water has been removed. If evaporated entirely to dryness, a portion of the

chlorate of ammonia would volatilize, and a portion be converted into sal ammoniac; the volatile products which separate are, besides water, chlorine, nitrous oxide, and oxygen.

2 at. $NH_4O + ClO_5$, form
1 at. $NH_4 + Cl$, 4 at. HO, 1 at. Cl, 1 at. NO, and 7 at. O.

Even in evaporating to the requisite point, a temperature higher than that of the water bath is carefully to be avoided. The whole of the chlorate of ammonia seldom escapes decomposition, but if the previous directions have been carefully followed the loss will be very inconsiderable. In order to re-obtain the alcohol with which the pasty mass is treated, the spirituous solution is mixed with water and distilled, and the aqueous solution of chlorate of baryta converted by caustic baryta, with the aid of a gentle heat, into chlorate of baryta and free ammonia.

1 at. $NH_4O + ClO_5$, and 1 at. BaO, form
1 at. $BaO + ClO_5 + HO$, and 1 at. NH_3.

The baryta solution employed, is that obtained by treating the residue, after heating together either sulphuret of barium and oxide of copper, or nitrate of baryta and iron filings. To avoid any loss, an excess of baryta water is employed, which when no more ammonia is given off imparts an alkaline reaction to the solution, and is, during the evaporation of the liquid to dryness, entirely or mostly converted into insoluble carbonate of baryta. If on resolution the salt has an alkaline reaction, and contains caustic baryta, a stream of carbonic acid is passed through to neutralize the latter. The carbonate of baryta having scarcely any action on the chlorate of ammonia cannot be employed for its decomposition. The decomposition of the chlorate of ammonia by baryta always causes the formation

of a small quantity of sal ammoniac, and from the latter a little chloride of barium, which, however, by crystallization remains in the last portions of the mother liquor.

The alcohol re-obtained generally possesses a slight odour of chloric ether and an acid reaction (from the decomposition of a small portion of the chlorate of ammonia during the distillation, and the consequent action of the liberated chlorine): it is nevertheless applicable to many purposes, for instance, in making the Spiritus salis dulcis.

Properties.—Chlorate of baryta crystallizes in colourless four-sided prisms, is odourless, of a pungent saline, somewhat cooling taste, and unalterable in the air. When heated it first loses its water, then fuses, and frothing up gives off oxygen, the last portion with a slight explosion; it now becomes dry, and is converted entirely into chloride of barium, which at a strong red heat liquefies without further change. It dissolves in 3 parts of cold and equal parts of boiling water, the solution has a neutral reaction. Alcohol of 80 per ct. dissolves at the ordinary temperature only $\frac{1}{169}$, when boiling $\frac{1}{36}$ of its weight. *Chloride of barium* is known by its white precipitate with nitrate of silver; *ammonia* by the odour evolved with caustic potash; and *caustic baryta* from its alkaline reaction.

BARIUM OXIDATUM NITRICUM.

Barytæ Nitras.—Baryta Nitrica.—Nitrate of Baryta.

FORMULA: $BaO + NO_5$.

Preparation.—Sulphuret of barium is mixed, with constant stirring, in twelve times its weight of distilled water, in a capacious earthen dish, and nitric acid spec. grav. 1·20 diluted with twice its volume

of water gradually added, until it scarcely causes an effervescence and the liquid renders turmeric paper only slightly brown. I used on an average 6 parts of acid, spec. grav. 1·20, to the sulphuret of barium from 5 parts of heavy spar. It is then treated just as for chloride of barium, the solution is filtered, saturated with nitric acid, and crystallized. The 5 parts of heavy spar gave generally 3 of nitrate of baryta.

Recapitulation.—As with chloride of barium :—

1 at. BaS, 1 at. NO_5, and 1 at. HO, form
1 at. $BaO + NO_5$, and 1 at. HS.

The quantity of acid required is uncertain, being dependent on the greater or less reduction of the heavy spar by charcoal. As the nitrate of baryta is more difficultly soluble in water than the chloride of barium, the sulphuret is to be treated with a larger portion of water. The nitric acid must also not be concentrated, otherwise it may react on the sulphuret, converting it into sulphate of baryta.

Properties.—Nitrate of baryta crystallizes in transparent permanent octahedra and tetrahedra, is odourless, of a pungent and slightly bitter taste, soluble in 14 parts of water at the ordinary temperature, in 3 of boiling water, and slightly in alcohol. Heated it fuses gradually, evolving acid, which as quickly decomposes into oxygen and hyponitric acid. For impurities test as in the chloride, and for chlorine with nitrate of silver.

BERBERINUM MURIATICUM.

Berberini Hydrochloras.—Hydrochlorate of Berberine.

FORMULA : $C_{42}H_{18}NO_9 + HCl + HO$.

Preparation.—25 Parts of fresh or 10 parts of dry barberry root bark are finely sliced, and boiled

for 2 hours with 100 parts of water in a copper kettle, strained, the residue pressed, and the boiling, &c., repeated twice again, but with only 60 parts of water; the liquids evaporated over a naked fire to a thin syrup, then in a copper still, heated by a water bath, to the consistence of a stiff extract; to this whilst hot is added, with constant stirring, 10 parts of alcohol, of 90 per ct., the still head replaced, and a gentle heat kept up for one day. When it has digested in the cold for two more days, the spirituous solution is poured off from the dark brown mass, and the latter digested with 5 parts of alcohol, of 90 per ct.; both solutions are then returned to the still (which has in the mean time been emptied), 2 parts of water are added, and so much alcohol drawn off as shall leave a residue equalling 4 parts; this is emptied into an earthen dish, the latter covered and placed in a cool spot. By the following day the whole mass (if not solidified) is generally full of very fine yellow needles; it is, however, better to wait at least a week before collecting the berberine. It is then placed on a thick linen strainer, well pressed, a little cold water added, and again pressed, and for medical purposes dried at once with a gentle heat, or else dissolved in a little hot water and crystallized. The yield is ordinarily about 1 per ct. of the fresh bark.

The mother liquors scarcely yield enough berberine on evaporation to pay for collecting; they nevertheless contain an appreciable quantity, which separates after standing something like a year. It is best to evaporate them to a thick syrup and stand the latter in a cool place; at the end of about a twelvemonth the extract is treated with 3 or 4 times its weight of water, the berberine strained off, and purified by solution in boiling water and crystallization; the mother liquors now obtained may be used for oxycanthin. The berberine may be more

quickly obtained from the mother liquors by treating it with hydrochloric acid to a strongly acid reaction, letting it stand some days, pressing the pasty mass, washing it with cold and then dissolving in hot water, neutralizing the acid with some ammonia, and placing the solution to crystallize in a cool place.

Recapitulation.—Berberine is not, as was formerly supposed, an acid colouring matter, but a true alkaloid, existing in the Barberry (Berberis Vulgaris, L.) as a chloride (at least it is obtained in the preceding method as such), and imparting to those portions of the plant impregnated with it a beautiful yellow colour; its distribution is not equal, the rind of the root being richest in it, and of course to be preferred for its extraction; the best time for collecting it is August. Besides the colouring matter, water dissolves a quantity of extractive matter, to remove which the treatment with strong alcohol is resorted to, the latter dissolving only the berberin, the purification of which depends on its ready solubility in hot alcohol or water, and difficult solubility in cold.

Properties.—Pure chloride of berberin is a light fine crystalline powder, of a clear yellow colour, consisting of silky needles, odourless, of a strong, pure and persistent bitter taste. Water at the ordinary temperature dissolves $\frac{1}{500}$; alcohol of 80 per ct. $\frac{1}{250}$; both take it up in almost any quantity when boiling. In ether it is insoluble. It is not volatile, but when heated decomposes, forming empyreumatic vapours, having an alkaline reaction, and leaving a carbonaceous residue, which is consumed entirely, but with difficulty, on heating.

BISMUTHUM OXIDATUM NITRICUM BASICUM.

Bismuthi Subnitras.—Magistery of Bismuth.—Subnitrate of Bismuth.

FORMULA: $4Bi_2O_3 + 3NO_5 + 9HO$.

Preparation.—A glass flask is about half filled with a known quantity of nitric acid of spec. grav. 1·20, and metallic bismuth, in pieces about the size of lentils, gradually added, allowing one portion entirely to dissolve before adding more; and when there is no longer a perceptible action, the flask is placed in warm sand, the addition of the metal continued until it is no longer affected, but becomes covered with a white crust. 4 Parts of acid, of the proper strength, dissolve about 1 part of metal. The solution, generally of a yellowish-green colour, is mixed with the half of its weight of pure water, then allowed to deposit the flocculent grayish matter it contains, which with the remaining portion of metal are separated by decantation and filtration. The clear liquid is now poured, with constant stirring, into pure water six times the weight of the acid employed. When entirely precipitated, the supernatant acid liquid is decanted, the white residue thrown on a filter, and when nothing more drops it is washed with as much water as was used to dilute the acid solution, and with which the precipitating vessel has been rinsed to remove any adhering portions. It is again drained, the contents of the filter spread on blotting paper, several folds thick, dried in the sun or with a very gentle heat, and kept in a closed bottle. The product will be about equal to the metal used.

If the bismuth contains arsenic (which may be determined by the blowpipe), the nitric acid solu-

tion must be boiled with caustic potash; the yellow precipitate of oxide of bismuth thus formed is well washed, again dissolved in nitric acid, and the solution then precipitated with water.

Recapitulation.—The metallic bismuth will be very readily acted on and dissolved by nitric acid, a portion of the acid being decomposed into oxygen, which combines with the metal, and nitric oxide, $=NO_2$, which in the air again instantly attracts oxygen, and passes off as brownish-yellow vapours of hyponitric acid, $=NO_4$; the oxidized metal combining with the remainder of the nitric acid.

2 at. Bi, and 4 at. NO_5, form
1 at. $Bi_2O_3 + 3NO_5$, and 1 at. NO_2; further
1 at. NO_2, and 2 at. O, form
1 at. NO_4.

2660 Parts of bismuth require 2700 parts of anhydrous, or 10000 parts of nitric acid, spec. grav. 1·20 (=27 per ct. acid). Most of the metal may be dissolved without the application of heat, and by this means a waste of acid is prevented; and only when there is no more action in the cold, heat is resorted to. The metal must only be added gradually, or the action will be so violent as to fracture the flask, or cause the acid to boil over; and at the same time a basic salt will be formed, especially when the acid is partially saturated, which can with difficulty be redissolved. The yellowish-green colour of the solution arises from iron or copper, and the gray flakes which separate during the solution are sulphur (present as sulphuret of bismuth), to remove which the liquid is diluted, allowed to subside, and filtered. When the clear solution comes in contact with a large quantity of water, a basic salt precipitates, as a snow-white, silvery, glistening crystalline powder, and an acid salt remains in solution. The quantity of the precipitate increases with the water added,

until it has reached 16 times that of the acid used, at which point all the neutral salt is converted into acid and basic salts. The precipitate formed, from the first to the last, has entirely the same composition, viz. — as Dulk has shown — $Bi_2O_3 + NO_5 + 2HO$, and is thus exemplified :—

2 at. $Bi_2O_3 + 3NO_5$, and xHO, form
3 at. $Bi_2O_3 + NO_5 + 2HO$, the precipitate,
1 at. $Bi_2O_3 + 9NO_5 + xHO$, the acid solution.

10640 Parts of bismuth (8 at.) should, excluding all possible loss, yield 11580 parts of precipitate. This if the pharmacopœia* process is followed will never be obtained, as it directs that the precipitate after pouring off the supernatant acid liquor should again be washed with pure water, and then dried; this causes a further decomposition of the basic salt, oxide of bismuth with a larger proportion of acid being separated, and a still lower basic salt being formed. If washed only as much as I have directed, the preparation has the composition ascribed to it at the head of this article $= 4Bi_2O_3 + 3NO_5 + 9HO$, and contains in 100 parts $79{\cdot}5Bi_2O_3$, $13{\cdot}6NO_5$ and $6{\cdot}9HO$. With more washing it is still further decomposed, finally leaving only oxide of bismuth; it is therefore an error to continue the washing so long as an acid liquid passes off.

I cannot recommend that the bismuth solution be crystallized previous to precipitation; it is a troublesome operation, and the extra quantity of subnitrate thus formed is not so great as might be expected.

In the acid solution will be found all the other metals present, as iron, copper, lead, &c.; they are precipitated with lime, and the hydrated oxide of

* The Bavarian Pharmacopœia is here indicated.

bismuth thus obtained = $Bi_2O_3 + HO$, reserved for the next preparation of subnitrate.

When arsenic is present it is necessary to use a special method for its separation, otherwise it would in a remarkable manner be thrown down with the bismuth. Caustic potash readily dissolves the arsenious acid, leaving the pure oxide of bismuth, which is then treated as the metal, dissolved in acid and precipitated with water. The nitrate of potash obtained as a secondary product is applicable to the manufacture of nitric acid.

Properties.—The subnitrate of bismuth is obtained from a cold solution of the nitrate as a snow-white, silvery, glistening crystalline powder, which under the magnifying glass exhibits an aggregation of transparent prisms. It is odourless and tasteless. Exposed to the sunlight it undergoes no change of colour. Heated it does not fuse, but becomes first yellow and then brown, nitric acid being evolved; on cooling, the brown colour is replaced by lemon yellow (pure oxide). By shaking with water a portion of acid and oxide is taken up, leaving a still more basic salt, the water at the same time acquires an acid reaction and the property of decolourizing indigo. In dilute nitric acid it must dissolve readily and completely, if with effervescence some *carbonate* is present, probably *carbonate of bismuth* or *carbonate of lime*, both of which I have found in the commercial salt. Lime is detected by the turbidity which oxalate of ammonia causes in a filtered solution of the salt after precipitation with ammonia. If the solution in nitric acid gives a precipitate with nitrate of silver, it is not free from *chlorine*, which is due to the use either of impure nitric acid or impure water. From similar causes sulphuric acid may be present and will be detected by nitrate of baryta. A white precipitate caused by sulphate of soda indicates *lead*, which is sometimes present in commercial bismuth, and by throwing down the nitrate with

common water (not free from sulphates), it is precipitated with the bismuth. If the solution in nitric acid is reddened by sulphocyanide of potassium, it contains peroxide of iron; a solution of sulphocyanide of iron is formed, which is soluble.

1 at. $Fe_2O_3 + 3NO_5$, and 3 at. $KCyS_2$, form
1 at. $2Fe + 3CyS_2$ and 3 at. $KO + NO5$.

If in addition to the white precipitate ammonia in excess causes a blue colour, it is contaminated with *copper*. In testing with nitrates of silver and baryta or sulphate of soda, it must be borne in mind that water alone would cause a precipitate in the solution of the nitrate of bismuth, and consequently these aqueous solutions are only to be added by drops. As the nitric acid present interferes with the detection of arsenic on charcoal, it is better to employ Marsh's apparatus (*vide* Acid, Muriat.), adding about as much of the nitrate as the point of a knife will hold, to the sulphuric acid and zinc. Should the preparation acquire a gray colour by exposure to the light, silver may be present, though it is more probably due to the action of sulphuretted hydrogen, and the formation of sulphuret of bismuth, from the bottle not being well closed.

BRUCINUM.

Brucine.

Formula: $C_{16}H_{26}N_2O_8 + 10HO = Br + 10HO$.

Preparation.—From Nux Vomica.—Rasped nux vomica is digested for one day in a copper still with five times its weight of alcohol of 40 per ct. at a gentle temperature, the residue strained through linen, the residue pressed, and twice again treated in the same manner with water. The collected

expressed liquors are returned to the still when cleansed, the alcohol drawn over, the residual brown liquid poured into a copper vessel and diluted until its weight equals that of the nux vomica used; then, in an earthen vessel, add to it a solution of sugar of lead so long as a precipitate is formed. About $\frac{1}{50}$ the weight of the nux vomica will be required of sugar of lead. The precipitate is filtered, the solution evaporated to about half, and when cool, calcined magnesia $\frac{1}{30}$ the weight of the nux vomica is added to it; it is now allowed to remain for a week, with frequent stirring, at the ordinary temperature, thrown on a filter, washed once with a little water, and dried. When the dried precipitate has been powdered, it must be exhausted three times with alcohol of 80 per ct., and distilled from the filtered tincture, so that about $\frac{1}{50}$ the weight of the nux vomica remains. At the bottom of the retort there will be a white crust, and above it a yellowish liquid. The supernatant liquid is carefully poured off, the solid portion softened with alcohol of 40 per ct., then thrown on a filter and washed with alcohol of a similar strength (which may afterwards be used to rinse out the retort), so long as the liquid passing through is coloured red by nitric acid. The contents of the filter are dried and kept as Strychnine, whilst the collected spirituous solutions, for the preparation of pure brucine, are treated as follows:—

Powdered binoxalate of potash, equalling in weight $\frac{1}{50}$ that of the powdered nux vomica is added, and the spirituous solution carefully evaporated to dryness (if the mass remains tough add some charcoal powder), the dry mass is rubbed to a fine powder, agitated with four times its volume of absolute alcohol in a closed vessel, at a temperature as near 32° Fah. as possible, for two days, thrown on a filter, and washed with alcohol of the same strength until the liquid passes off clear; it is then

dissolved in warm water, heated until every trace of alcohol has passed off, and agitated for several days at the ordinary temperature with calcined magnesia the weight of the nux vomica. The insoluble portion is collected in a filter, and when thoroughly drained, digested with alcohol of 90 per ct., filtered and rinsed with alcohol. The alcoholic solution, carefully evaporated, is set in a cool place, and will soon form an oleaginous layer at the bottom, which gradually becomes a crystalline mass; this, after separating the mother liquor, which may be further evaporated, is dried at a moderate temperature. To obtain the brucine in larger crystals, it is dissolved in the smallest quantity of alcohol of 90 per ct., and subjected to spontaneous evaporation. The yield from ten pounds avoirdupois of nux vomica is about 6 drachms of brucine and as much strychnine.

Recapitulation.—Both brucine and strychnine exist in the nux vomica in combination with an acid, the nature of which is not perfectly understood: according to some it is a peculiar acid (Igasuric acid), according to others Lactic acid. Weak alcohol takes up both salts, together with extractive matter. Acetate of lead throws down from the solution, deprived of its alcohol, a great quantity of the colouring matter combined with the lead, leaving the acetic acid free. One portion of the calcined magnesia saturates this free acid, another decomposes the salt of the alcaloid, combining with its acid, and precipitating the base, which is soluble in water only in excessively minute proportions. From the precipitate formed on agitation with magnesia, alcohol takes up the alkaloid, leaving behind the excess of magnesia. On distilling, the strychnine first separates, leaving scarcely any but brucine in the mother liquor. The latter is contaminated with colouring matter; binoxalate of potash converts the brucine into oxalate, and this when treated with absolute alcohol at 32° Fah.

remains unacted on, whilst the colouring matter dissolves. The rest of the treatment so much resembles the preceding as to require no further explanation.

Properties.—Brucine slowly crystallized forms colourless four-sided prisms, which however have generally a tinge of yellow, and from long exposure to the air acquire an opaque surface. Heated it melts, loses its water, and forms, on cooling, an amorphous wax-like mass, which at a higher temperature must burn without residue. Cold water dissolves $\frac{1}{800}$ of brucine; alcohol, even when weak, readily takes it up; its solutions have an intensely bitter taste, ether is without action on it. In chlorine water the brucine entirely dissolves (being decomposed), assuming a rose colour, which ammonia converts to a dirty yellow. Nitric acid dissolves it (also with decomposition), forming a deep rose colour, which on warming becomes yellow, and if protrochloride of tin is now added, a purple violet colour and precipitate are formed. The presence of strychnine is known when the alkaloid dissolved in alcohol is treated with an alcoholic solution of indigotic acid, and to the yellow precipitate, after subsidence and decantation, is added acetic acid. If entirely soluble in this menstruum, the brucine is free from strychnine, but a residue denotes strychnine. The nature of this precipitate requires investigation.

CADMIUM OXIDATUM CARBONICUM.

Carbonate of Cadmium.

FORMULA: $CdO + CO_2$.

Preparation.—Metallic Cadmium in small portions is added to nitric acid spec. grav. 1·20 in a glass flask, so long as it is dissolved; the application of heat is unnecessary. 1 Part of cadmium dissolves

in 5 parts of acid having the above strength. The solution is diluted with ten times its weight of distilled water, and carbonate of ammonia added so long as a precipitate is formed. Nearly $1\frac{1}{2}$ parts of this salt are requisite. When the precipitate has subsided it is collected in a filter, washed with distilled water and dried at a gentle heat. It yields nearly 3 parts.

Recapitulation.—Nitric acid dissolves cadmium in the cold with the greatest facility, yellowish-brown vapours being evolved. The vapours arise from one part of the acid giving up 3 atoms of oxygen to oxidize the metal, and the ensuing nitric oxide $= NO_2$ attracting, so soon as it comes in contact with the air, 2 more atoms of oxygen, and forming hyponitric acid $= NO_4$. The oxidized cadmium combines with the remaining nitric acid.

3 at. Cd, and 4 at. NO_5, form
3 at. $CdO + NO_5$ and 1 at. NO_2.

2100 Parts of cadmium require 2700 parts of anhydrous acid, or 10000 parts of acid having a spec. grav. 1·20 (which contains 73 per ct. of water). The ordinary sesquicarbonate of ammonia decomposes the metallic nitrate, giving off carbonic acid and forming insoluble carbonate of cadmium and readily soluble nitrate of ammonia.

2 at. $CdO + NO_5$, and 1 at. $2\,NH_4O + 3\,CO_2$, form
2 at. $CdO + CO_2$, 2 at. $NH_4O + NO_5$, and 1 at. CO_2.

To 1400 parts of the metal 1475 parts of carbonate of ammonia are necessary, if the latter contains no bicarbonate; but as this is generally present more is usually required.

Properties.—Carbonate of cadmium is an odourless and tasteless snow-white powder, soluble in almost all acids but not in water. Heated, it loses its

carbonic acid, leaving a brown powder (pure oxide), unalterable by heat; but heated on charcoal before the blowpipe it entirely volatilizes and gives the charcoal a brown coating. The carbon abstracts its oxygen to form carbonic acid, the reduced metal volatilizing at a red heat again becomes oxidised as soon as it reaches the outer blowpipe flame, and is redeposited on the charcoal. In testing for other metals follow the directions given for oxide of zinc. If a solution of it in hydrochloric acid supersaturated with carbonate of ammonia, filtered from the precipitate and treated with hydrosulphuret of ammonia, gives a white precipitate, *zinc* is present; the oxide of zinc is soluble in excess of carbonate of ammonia and precipitates on the addition of hydrosulphuret of ammonia as a white sulphuret of zinc. When free from copper or lead the acid solution very much diluted must yield with excess of sulphuretted hydrogen gas a pure yellow precipitate of sulphuret of cadmium, and the filtered liquid undergoes no change when treated with ammonia; if, however, this or hydrosulphuret of ammonia cause a white turbidness, zinc is present, and a grey precipitate denotes iron.

CALCIUM CHLORATUM.

Calcii Chloridum.—*Chloride of Calcium.*—*Muriate of Lime.*

FORMULA OF THE FUSED: $CaCl$.
FORMULA OF THE DRIED: $CaCl + 2HO$.
FORMULA OF THE CRYSTALLINE: $CaCl + 2HO + 4Aq$

Preparation.—The basis of all three preparations is the residue on making caustic ammonia. This is treated with water boiled for some time, allowed to settle, decanted and strained, the clear liquid is

evaporated to dryness in an iron pot, and heated until it becomes liquid in an iron dish, then returned to the iron pot, which has been cleaned and dried, powdered so soon as it has solidified, and kept in a well-closed bottle. For most purposes the common chloride of calcium is sufficiently pure. To prepare the other two hydrated salts, one part of the dried is dissolved in three parts of water, filtered from the precipitate (which is always present), the alkaline reaction neutralized with a few drops of hydrochloric acid, and evaporated in a porcelain dish either to crystallization or dryness. The crystals (freed between blotting paper from adhering liquid,) and the dried salt must both be preserved in well-closed bottles from access of the air.

When perfectly pure preparations are required, the common anhydrous (fused) chloride of calcium is exhausted with alcohol of 80 per ct., filtered, and to the filtrate so much distilled water added as equals the weight of the chloride of calcium, the alcohol distilled off, the alkaline residue neutralized with hydrochloric acid, evaporated in a porcelain dish to dryness and the mass fused in a porcelain crucible, from which pure anhydrous chloride of calcium, the two pure hydrated salts are obtained.

If no ammonia residue is to be had, hydrate of lime is dissolved in common hydrochloric acid, taking care the lime is in excess, digested some days, frequently shaking, the residue allowed to subside, and filtered; to the filtrate hydrochloric acid is added, drop by drop, until neutral, it is then evaporated to crystallization or dryness, &c. When the hydrochloric acid contains sulphuric, as is frequently the case, the salt must be dissolved in alcohol, if required perfectly pure.

Recapitulation.—The residue from the manufacture of caustic ammonia is really chloride of calcium with excess of lime. Water dissolves the chloride of calcium and a little free lime, the latter

imparting an alkaline reaction to the solution; and on account of this free lime the other bases present (magnesia and alumina from the lime oxide of iron from the lime and sal ammonic, oxide of copper and tin from the still in which the caustic ammonia was prepared) do not dissolve, whilst any ammonia is driven off. By evaporation to dryness the clear solution attracts carbonic acid from the air and gives on redissolving a precipitate of carbonate of lime; a portion of lime however always remains free, on which account the neutralization with hydrochloric acid is prescribed.

The treatment with alcohol is to cause the separation of sulphate of lime, almost always contained in the common chloride of calcium. The other manipulation requires no explanation. By treating with alcohol the sulphate of lime, always present in common chloride of calcium, is precipitated.

In making it direct from lime and hydrochloric acid, an excess of the former must be used to prevent the solution of the magnesia, alumina and iron, exactly as in the first method.

Properties.—Pure chloride of calcium, in its fused (anhydrous) state, forms a hard white mass, when dried a white crystalline powder, and crystallized 4 and 6 sided fluted prisms, tasting somewhat like sulphate of magnesia; it is odourless, and attracting water from the air with avidity, deliquesces. In water, as in alcohol, it is very soluble; the solution should have no action on litmus or turmeric paper. If ammonia causes in its solution a white precipitate soluble in muriate of ammonia, *magnesia* is present; this base has a great affinity for salts of ammonia, forming with them double salts; when, therefore, in its freshly-precipitated state it comes in contact with sal ammoniac, it drives out a portion of the base, forming chloride of magnesium, which combines with the excess of chloride of ammonium to a double salt.

1 at. MgO, and 2 at. NH_4Cl, form
1 at. $NH_4Cl + MgCl$, 1 at. NH_3, and 1 at. HO.

If the white ammoniacal precipitate is soluble in caustic potash, but not in muriate of ammonia, it is *alumina*. If the precipitate is yellow or brown, and not entirely soluble in sal ammoniac or caustic potash, it contains *oxide of iron*. If on addition of ammonia the solution of chloride of calcium acquires a blue colour, it denotes *oxide of copper*. A white precipitate, with chloride of barium, *sulphuric acid*.

CALCIUM OXIDATUM ACETICUM.

Calcis Acetas.—Acetate of Lime.

Formula of the Crystallized :

$$CaO + C_4H_3O_3 + HO.$$

Formula of the Dried :

$$CaO + C_4H_3O_3.$$

Preparation.—Concentrated acetic acid is gently warmed in a glass flask, in a sand bath, and hydrate of lime added so long as it is dissolved. 4 Parts of acid, spec. grav. 1·045 (=36 per ct. anhydrous acid) dissolve 1 part of hydrate of lime. Pure lime, equalling ⅛ of that already dissolved, is then added, the whole allowed to remain, frequently shaking, for two days, at the ordinary temperature, the residue filtered and washed with a little pure water, and this clear solution treated with just sufficient acetic acid to neutralize the alkaline reaction ; it is then evaporated with a very gentle heat to half. The crystals which form after some days are collected on a filter, and dried without heat on blotting paper. The mother liquor is still further

evaporated and crystallized. The weight of salt is about double that of the lime used.

Recapitulation.—Hydrate of lime is readily, and, if not too impure, entirely taken up by acetic acid. By warming, the thorough saturation of the acid is ensured:

1 at. $CaO + HO$, and 1 at. $C_4H_3O_3$, form
1 at. $CaO + C_4H_3O_3$, and 1 at. HO.

463 Parts of hydrate of lime require 638 parts of anhydrous or 1772 parts of acetic acid with 64 per ct. water. The excess of lime causes the precipitation of any magnesia, oxide of iron, or alumina that may be present in common lime. The solution, by taking up some free lime, acquires an alkaline reaction, on which account it must, after filtration, be again neutralized with a little acetic acid. It is difficult to obtain good crystals, and also to separate the crystals from the mother liquor, as they absorb it like a sponge; the only methods are to strain and press the salt, or to dry it direct.

Properties.—Acetate of lime crystallizes in silky glistening needles, which smell feebly of acetic acid, and possess a pungent, bitterish, warm taste. Exposed to the air they become white from loss of water, and must therefore be kept in a closed vessel. In water the salt dissolves readily, in alcohol with more difficulty. The solution has a neutral reaction. If it has a yellow colour, the acetic acid was possibly contaminated with *empyreumatic matter*, which may be determined by the smell. Any contamination with *acetate of lead* may be detected by chromate of potash, with which it gives a yellow precipitate of chromate of lead. The other tests are similar to those for chloride of potassium.

CALCIUM OXIDATUM CARBONICUM.

Calcis Carbonas.—Carbonate of Lime.

FORMULA: $CaO + CO_2$.

Preparation.—7 Parts of purified chloride of calcium are dissolved in 8 times their quantity of distilled water; 10 parts of liquor ammonia, 0·960 spec. grav., are diluted with 10 parts of distilled water, and in this are dissolved 5 parts of powdered carbonate of ammonia; the last solution is poured to the first with continued stirring, a small portion is filtered off, and if carbonate of ammonia renders the solution turbid a fresh quantity of carbonate of ammonia is added. When thoroughly precipitated the supernatant liquor is decanted, the residue collected on a filter or strainer, and washed until the liquid passing off gives no precipitate with nitrate of silver; it is then dried with a gentle heat. 7 Parts of chloride of calcium yield about 6 parts.

Recapitulation.—When solutions of chloride of calcium and ordinary carbonate of ammonia are brought together, the oxygen of oxide of ammonium passes to the calcium; the lime thus formed precipitates in combination with carbonic acid; the ammonium unites with the chlorine to readily soluble sal ammoniac, and the excess of carbonic acid escapes with effervescence. The reason of this effervescence is that the carbonate of ammonia when freshly prepared contains $1\frac{1}{2}$ at. of acid to 1 at. of base, whilst if much exposed to the air it acquires 2 at. In order to save this second at. of acid caustic ammonia is prescribed, which, combining with it, reacts on the chloride of barium solution. If we suppose, as is generally the case, that the sesquicarbonate of ammonia has partially or

entirely become bicarbonate, the following formula explains the process:

2 at. CaCl, 1 at. $NH_4O + 2CO_2 + HO$, and 1 at. NH_3, form
2 at. $CaO + CO_2$, and 2 at. NH_4Cl.

1386 Parts of anhydrous chloride of calcium require 988 parts of bicarbonate of ammonia, and 2130 of liquid ammonia.

The supernatant liquor will serve on evaporation for chloride of ammonium, but on account of a little chloride of calcium it contains, it can only be used for making liquor ammonia. The carbonate of ammonia must not be replaced by carbonate of potash or soda, if the preparation is required free from alkali.

Properties.—Pure carbonate of lime is an odourless, tasteless, snow-white crystalline powder. Heated to low redness it undergoes no change; at a higher temperature it loses a little carbonic acid, which is entirely given off if during the heating the powder be moistened from time to time with water. Its solution in hydrochloric acid should sustain no change with nitrate of silver, ferrocyanide of potassium, or ammonia in excess; if in the first instance a white precipitate falls, a *chloride* is present; in the second a blue or brown precipitate, *iron* or *copper;* in the third a brown precipitate, or blue colour, *iron* or *copper*. If in the nitric acid solution, neutralized by excess of the carbonate of lime, ammonia causes a white precipitate, soluble on the addition of sal ammoniac, *Magnesia* is present (*vide* CALCIUM CHLORATUM); if soluble in caustic potash, *Alumina*. A blackening with hydrosulphuret of ammonia indicates *metals*. *Sulphuric acid* is determined by a baryta salt. To detect *potash* or *soda*, supersaturate the nitric acid solution with ammonia, entirely precipitate the lime with oxalate of ammonia, and evaporate the filtered solution to dryness,

then dissolve the residue in water; to one portion add tartaric acid in excess, which will throw down with potash a difficultly-soluble crystalline precipitate of bitartrate of potash; the remainder of the solution is evaporated to dryness, and heated to redness on a platinum wire, when any soda will give an intense yellow to the outer flame of the blowpipe.

CALCIUM OXIDATUM SULPHURICUM.

Calcis Sulphas.—Gypsum Purum.—Sulphate of Lime.—Pure Gypsum.

FORMULA: $CaO + SO_3 + 2HO$.

Preparation.—Chloride of calcium is dissolved in eight times its weight of distilled water, and a solution of Glauber's salts, one part to eight, added so long as a precipitate forms. 1 Part of anhydrous chloride of calcium requires 3 parts of crystallized sulphate of soda. The precipitate when deposited is collected on a filter, washed with cold distilled water so long as the filtered liquid yields a precipitate or turbidity with nitrate of silver, and dried at a gentle heat. 3 Parts of anhydrous chloride of calcium yield about 4 parts of precipitate.

Recapitulation.—Chloride of calcium and sulphate of soda in aqueous solution exchange elements, forming insoluble sulphate of lime, which falls in combination with two atoms of water, and readily soluble chloride of sodium:

1 at. $CaCl$, and 1 at. $NaO + SO_3 + 10HO$, form
1 at. $CaO + SO_3 + 2HO$, 1 at. $NaCl$, and 8 at. HO.

693 Parts of chloride of calcium require 2015 parts of crystallized sulphate of soda. On account of the washing necessary to remove the chloride of sodium, a small quantity of the sulphate of lime is

lost. Hot water must not be used, as otherwise the solubility of the sulphate of lime, on account of the chloride of sodium it contains, will be increased.

Properties.—The sulphate of lime obtained by precipitation is a light white powder, consisting of fine needles, possessing neither smell nor taste, and in appearance somewhat resembling sulphate of quinine. 332 Parts of water dissolve 1 part; the solution has a neutral reaction; it is not more soluble in boiling water, and is insoluble in alcohol. Heated a little above 212° Fah. it loses its water, but takes it up again if moistened with it, heat being evolved. On this property depends the formation of plaster-of-paris casts. This evolution of heat is due to a portion of the water passing from the liquid to the solid state. If gypsum is heated to redness it loses the property of chemically combining with water (hardening with water), it is, to use the common expression, "burnt to death;" it has not, however, lost its solubility in water, and its aqueous solution, evaporated to dryness, and heated gently, still possesses the properties of the crystallized (hydrated) gypsum. Nitrate of silver, ammonia, ferrocyanide of potassium, and hydrosulphuret of ammonia, cause no change in its solution; *Vide* CALC. CARBON).

CALCIUM SULPHURATUM.

Calcii Sulphidum.—Sulphuret of Lime.

FORMULA: CaS; or,
$3CaS + (CaO + SO_3)$.

Preparation.—(*a*) *The pure.*—3 Parts of finely-powdered crystallized sulphate of lime (native gypsum), are intimately mixed with 1 part of finely powdered wood charcoal, the mixture well

pressed into an earthen or black lead crucible, covered with a thin layer of charcoal powder, and the cover luted with the exception of a very small opening on the top; when the luting is dry, heat is applied, at first gently, and afterwards strongly, in a good wind furnace for at least one hour. When entirely cooled, the crucible is removed, the upper portion of the contents taken off, the remainder powdered in a mortar, and kept in a well-closed vessel. The yield is nearly $1\frac{1}{2}$ parts.

(*b*) *That containing Gypsum.*—2 Parts of hydrate of lime are intimately mixed with 1 part of powdered sulphur, placed in a crucible with a thin layer of hydrate of lime at the top, the crucible closed, as in (*a*), and heated in a moderate fire until at the upper part of the crucible no sulphur flames are visible. The fire is then increased, the crucible brought to a red heat, and so continued for an hour. Otherwise proceed as with (*a*). $2\frac{1}{3}$ Parts of sulphuret of calcium are the product. Or, 3 parts of finely-powdered carbonate of lime (chalk), and 1 part of sulphur, are treated in the same way, and yield $2\frac{3}{4}$ parts.

To obtain a good preparation, not more than 2 pounds of the material should be heated at once.

Recapitulation (*a*).—The native gypsum, a compound of 1 at. lime, 1 at. sulphuric acid, and 2 at. water, loses its water when moderately heated; at a still higher temperature the carbon abstracts from it all its oxygen, which, from excess of the former, passes off as carbonic oxide, sulphuret of calcium forming the residue.

1 at. $CaO + SO_3 + 2HO$, and 4 at. C, form
1 at. CaS, 4 at. CO, and 2 at. HO.

1075 Parts of hydrated sulphate of lime require 300 of pure carbon, but on account of impurities in wood charcoal, somewhat more is necessary. If the gypsum contains iron and manganese, as is

generally the case, these metals are converted from sulphates into sulphurets. The superficial layer of charcoal is to prevent the oxidizing action of the air.

(*b*) By heating the hydrate of lime with sulphur, the water of the hydrate of lime is first given off, then one portion of sulphur absorbs the greater portion of the oxygen combined with the lime, converting it into sulphuric acid, which unites with part of the lime, the remainder of the sulphur combining with the calcium to simple sulphuret of calcium:

4 at. $CaO + HO$, and 4 at. S, form
3 at. CaS, 1 at. $CaO\,SO_3$, and 4 at. HO.

1850 Parts of hydrate of lime require only 800 parts of sulphur, but rather more than this is used, a portion being volatilized during the reaction. The lime covering answers the same purpose as the charcoal.

In using carbonate of lime the process is exactly the same, only, instead of water, carbonic acid is given off. 2500 Parts of carbonate of lime require 800 parts of sulphur.

Properties.—Pure sulphuret of calcium is in reality a white powder, inclining more or less to red or gray (from the iron or manganese contained in the materials used), which is of no consequence in its application. That prepared according to the first process is gray, from the charcoal mixed with it. In the air it has a feeble smell of sulphuretted hydrogen. The reason of this is the water and carbonic acid contained in the air, which occasion the formation of sulphuretted hydrogen and carbonate of lime:

1 at. CaS, 1 at. HO, and 1 at. CO_2, form
1 at. $CaO + CO_2$, and 1 at. HS.

The quantity of sulphuretted hydrogen thus given

off is, however, inconsiderable, for at the same time, and far more energetically, the oxygen of the air acts not only on the calcium but also on the sulphur, forming hyposulphurous acid and lime. Half of the lime combines with the hyposulphurous acid, and the other half with the carbonic acid of the air.

2 at. CaS, 4 at. O, and 1 at. CO_2, form
1 at. CaO + 2 SO, and 1 at. CaO + CO_2.

When all the sulphuret of calcium is decomposed, the continued action of the oxygen of the air converts the neutral hyposulphite of lime into sulphur and sulphate of lime:

1 at. CaO + 2 SO, and 1 at. O, form
1 at. CaO + SO_3, and 1 at. S.

The final result of the action of the air on sulphuret of calcium is, therefore, carbonate of lime, sulphate of lime, and sulphur; or,

2 at. CaS, 1 at. CO_2, and 5 at. O, form
1 at. CaO + CO_2, 1 at. CaO + SO_3, and 1 at. S.

It requires some time to effect the entire decomposition.

Water takes up $\frac{1}{500}$ part its weight of sulphuret of calcium, the solution has a strong alkaline reaction, and hepatic taste. When the process (*b*) has been followed, it gives with chloride of barium a large precipitate of sulphate of baryta; but if the same occurs with that prepared by (*a*), the sulphate of lime has either not been entirely reduced, or, from access of the air, it has again oxidized. In the latter case, carbonate of lime will also be present. If on the addition of dilute hydrochloric acid to the sulphuret of calcium, an effervescence, without a smell of sulphuretted hydrogen, takes place, the sulphuret is all oxidized; if sulphuretted hydrogen is given off, it may be distinguished from carbonic acid by passing into lime water, in which carbonic acid causes a precipitate; or by boiling,

filtering, and well washing out all the sulphuret of calcium, and then treating with hydrochloric acid, which will give an effervescence.

CALCIUM SULPHURATUM HYDRATICUM.

Rusma Turcarum.—Massa Depilatoria.—Hydrated Sulphuret of Calcium.

FORMULA: $CaS + HS + xHO$.

Preparation.—1 Part of hydrate of lime is rubbed with 1½ parts of water to a fine creamy consistence, poured into a deep cylindrical glass, and with frequent stirring sulphuretted hydrogen is slowly passed in until in excess, which is known by the milk of lime exhibiting no white spots, and when shaken up giving off a strong odour of the gas. 3 Parts of sulphuret of iron and 18 parts of dilute sulphuric acid will be requisite. The grey mass is kept in a well-closed bottle.

Recapitulation.—When sulphuretted hydrogen and hydrate of lime come in contact, they exchange elements, the calcium combines with the sulphur to sulphuret of calcium, the hydrogen with oxygen forming water:

1 at. CaO, and 1 at. HS, form
1 at. CaS, and 1 at. HO.

463 Parts of hydrate of lime decompose 213 parts of sulphuretted hydrogen, evolved from 550 parts of sulphuret of iron. The sulphuret of calcium for want of sufficient water is formed but slowly, and in proportion as the lime dissolves, consequently the gas must not be too rapidly evolved. Under any circumstances a considerable portion of the gas will escape undecomposed, whilst another part remains dissolved in the mass, and these are reasons why the quantity of sulphuret of iron is more than doubled. The iron, always present in common lime, will be

converted into black sulphuret of iron, and impart a grey colour to the mass.

Properties.—The preparation forms a grey pasty mass smelling strongly of sulphuretted hydrogen, of a powerful alkaline reaction and hepatic taste. When it no longer possesses these properties, it is decomposed, from the action of the air (*vide* CALCIUM SULPHURATUM), and useless.

CALCIUM SULPHURATUM STIBIATUM.

Calcii Antimonio Sulphidum.—Sulphuret of Antimony and Sulphuret of Calcium.—Hoffmann's Antimonial Sulphuret of Calcium.

FORMULA OF THAT PREPARED IN THE DRY WAY:

$$CaS + Sb_2S_3,\ xCaO + SO_3,\ xCaO,\ xCaS + Sb_2S_5.$$

FORMULA OF THAT PREPARED IN THE WET WAY:

$$3CaS + Sb_2S_5,\ xCaO + Sb_2O_5,\ xCaO + HO.$$

Preparation.—(*a*) *By the dry method.*—4 Parts of hydrate of lime, 1 part of sulphur, and 1 part of native sulphuret of antimony, which altogether must not exceed 2 pounds in weight, are very finely powdered, intimately mixed, tightly pressed into an earthen or black lead crucible, covered with a thin layer of lime and the crucible covered and luted, all but a small opening; the heat is at first gently applied and then brought to redness for half an hour and allowed to cool. The brown pulverulent mass beneath the layer of lime is placed in a well-closed bottle. The yield is about 5 parts. Various formulas being given in the different pharmacopœias for this preparation, as many kinds are obtained; consequently each should employ the method of his own pharmacopœia. The above is the Bavarian.

(*b*) *The wet method.*—Some pharmacopœias direct

this preparation to be made by the wet method. 3 Parts of hydrate of lime are mixed in a porcelain dish with 2 parts of golden sulphuret of antimony, and 24 parts of water, the mixture with constant stirring evaporated to dryness. The pale yellow powder thus obtained must be kept in a well-closed bottle: it decomposes far more readily than that prepared by the method (*a*). In this preparation, also, the proportions of the different pharmacopœias vary.

Recapitulation.—(*a*) When hydrate of lime, sulphur, and sulphuret of antimony are heated together in their relative proportions, the latter takes up more sulphur, forming the highest sulphuret of antimony, and the remainder of the sulphur acts on the lime (as in calcium sulphuratum), forming sulphuret of calcium and sulphate of lime, the former of which combines with the highest sulphuret of antimony, forming a sulphur salt; the water of hydration of the lime is evolved:

4 at. CaO, 6 at. S, and 1 at. Sb_2S_3, form
1 at. $3CaS + Sb_2S_5$, and 1 at. $CaO + SO_3$.

1400 Parts of anhydrous or 1850 parts of hydrate of lime require 1200 parts of sulphur and 2212 parts of black sulphuret of antimony. That prepared according to the pharmacopœia cannot have this proportion as it contains far more lime. In the preceding proportion, containing an excess of lime, viz., 4 parts of hydrate of lime, 1 part of sulphur, and 1 of sulphuret of antimony, we find that these correspond to 19 at. of hydrate of lime = 8787 parts, 11 at. of sulphur = 2200 parts, and 1 at. of sulphuret of antimony = 2212 parts. The 11 at. of sulphur form with 11 at. of lime, $8\frac{1}{4}$ at. sulphuret of calcium (CaS) and $2\frac{3}{4}$ at. sulphate of lime ($CaO + SO_3$). A portion of this sulphuret of calcium combines with the sulphuret of antimony to a sulphur salt; the other part with a portion of the free lime to a basic

sulphuret of calcium, so that in reality we obtain: sulphuret of antimony and calcium = $xCaS + Sb_2S_3$, basic sulphuret of calcium = $CaS + xCaO$, sulphate of lime $CaO + SO_3$, and free lime = CaO. According to theory there should be none of the highest sulphuret of antimony = Sb_2S_5 formed when the ingredients are in the prescribed proportion, as the lime has a greater affinity for the sulphur at a red heat than the black sulphuret of antimony possesses, yet the above preparation is never free from the pentasulphuret; the probable reason of this is the contiguity and ready fusibility of the two substances, sulphur and sulphuret of antimony. It also happens that if the proportion of sulphur is greater than is necessary to convert all the lime into sulphuret of calcium, a large proportionate quantity of the highest sulphuret of antimony is formed; when however the sulphur is not sufficient for this purpose, sulphuret of calcium is formed at the expense of the sulphuret of antimony, which is converted into oxide:

1 at. Sb_2S_3, and 3 at. CaO, form
1 at. Sb_2O_3, and 3 at. CaS.

(*b*) If lime and the highest sulphuret of antimony (golden sulphuret) are boiled together in water in equivalent proportions, a part of the lime changes elements with part of the sulphide, forming antimonic acid and simple sulphuret of calcium; the former combines with the rest of the lime, the latter with the pentasulphuret of antimony. These compounds are antimoniate of lime = $CaO + Sb_2S_5$, and sulphuret of antimony and calcium = $3CaS + Sb_2S_5$.

18 at. CaO, and 8 at. Sb_2S_5, form
3 at. $CaO + Sb_2O_5$, and 5 at. $3CaS + Sb_2S_5$.

6300 Parts of anhydrous or 8325 parts of hydrate of lime require 20896 parts of the golden sulphuret. The proportion 3 parts of hydrate of lime and 2 of golden sulphuret corresponds to $8\frac{1}{2}$ at. of hydrate of

lime = 3932 parts and 1 at. of the golden sulphuret of antimony = 2612 parts; consequently, for 8 at. of the latter there are 68 at. of hydrate of lime; 68—18 = 50 at. of free hydrate of lime in the mixture, and to this circumstance the pale colour of this preparation, compared with the preceding, is due.

Properties.—(*a*) As prepared by fusion is a liver coloured powder of hepatic taste and smell. Cold water dissolves it but partially, and in small proportions; the solution is colourless, of a strong alkaline reaction; hydrochloric acid precipitates from it, with evolution of sulphuretted hydrogen, dark orange red flakes, which dissolve when heated with excess of acid, excepting a trifling quantity of sulphur. The aqueous solution really contains a basic compound of sulphuret of calcium and the lowest sulphuret of antimony; a little hydrochloric acid precipitates the latter, forming with the sulphuret of calcium sulphuretted hydrogen and chloride of calcium.

1 at. CaS, and 1 at. HCl, forms
1 at. CaCl, and 1 at. HS.

A larger quantity of hydrochloric acid dissolves sulphuret of antimony (evolving sulphuretted hydrogen).

1 at. Sb_2S_3, and 3 at. HCl, form
1 at. Sb_2Cl_3, and 3 at. HS.

The solution would be perfect, were not a trace of the compound of sulphuret of calcium and the highest sulphuret of antimony present, but this is decomposed by hydrochloric acid with the separation of a portion of its sulphur:

1 at. $3CaS + Sb_2S_5$, and 6 at. HCl, form
3 at. CaCl, 1 at. Sb_2Cl_3, 6 at. HS, and 2 at. S.

Hot water takes up a large portion of the preparation but not the whole of it; the solution is yellowish,

and by dilution with water forms a reddish-brown precipitate. This is occasioned by the decomposition of the concentrated (or rather neutral) solution of the compound of sulphuret of calcium and lowest sulphuret of antimony, by excess of water, into a very basic soluble salt (sulphuret of antimony and excess of sulphuret of calcium), and a very acid insoluble salt (sulphuret of calcium and sulphuret of antimony in excess). If the precipitate is entirely free from the supernatant liquor, it must, as it contains only the lower sulphuret of antimony, be quite soluble in warm hydrochloric acid. Exactly neutralized with hydrochloric acid, a strong effervescence and evolution of sulphuretted hydrogen ensues; in this case the basic sulphuret of calcium is dissolved, and with excess of acid and heat the sulphuret of antimony at first precipitated is again taken up, leaving perhaps a trace of sulphur (*vide supra*). If the preparation is not entirely excluded from the air, one portion of the sulphur is liberated as such, the remainder gradually oxidizing, forms sulphuric acid; the antimony becomes converted into oxide of antimony or antimonic acid; the calcium into lime which combines with carbonic, sulphuric, and antimonic acids. In this state hydrochloric acid causes an effervescence, but without an odour of sulphuretted hydrogen, or orange red precipitate (separation of sulphuret of antimony), being formed.

(*b*) The preparation by the moist way is a clear yellow powder of hepatic taste and smell. Cold and hot water dissolve from it sulphuret of antimony and calcium, together with free lime, leaving the excess of lime and antimoniate of lime. The solution is a pale yellow, of a strongly alkaline reaction; a little hydrochloric acid precipitates, with evolution of sulphuretted hydrogen, clear orange red flakes of the highest sulphuret of antimony:

1 at. $3CaS + Sb_2S_3$, and 3 at. ClH, form
3 at. CaCl, 3 at. HS, and 1 at. Sb_2S_5.

The precipitate dissolves when boiled with hydrochloric acid, with separation of sulphur which is precipitated :

1 at. Sb_2S_5, and 3 at. HCl, form
1 at. Sb_2Cl_3, 3 at. HS, and 2 at. S.

In the air the sulphur salt is gradually converted into sulphate of lime, carbonate of lime, antimoniate of lime, and free sulphur ; the excess of lime also absorbs carbonic acid ; the preparation no longer evolves sulphuretted hydrogen, but only carbonic acid when treated with hydrochloric acid, nor does it acquire an orange red colour (*vide supra*).

CANTHARIDINUM.

Cantharidine.

FORMULA : $C_{10}H_6O_4$.

Preparation.—Coarsely powdered Spanish flies are digested in a sand bath for a day with 4 parts of water, strained through linen, pressed, and twice again digested with 2 parts of water ; the strained liquid is allowed to settle for one day, the supernatant oil separated, and after adding wood charcoal $\frac{1}{10}$th the weight of the insects, evaporated to dryness in a water bath. The dry mass is powdered and treated with sulphuric ether so long as the solution yields on evaporation a laminated residue. This is effected most conveniently in a glass percolator of conical shape, the smaller end of which is closed with a piece of thick linen. The percolator is fitted with a cork into the neck of a bottle, the extract placed in it, and treated with ether, which will yield a yellowish tincture. The wider upper end of the glass tube is loosely closed with a cork. The scales after evaporation of the ether are treated with

cold alcohol of 80 per ct. for one day, frequently shaking, the alcohol is then poured off, the laminæ spread on blotting paper and dried in the air. One pound of Spanish flies yields from 20 to 30 grains of cantharidine.

Cantharidine may also be prepared by direct treatment of the Spanish flies with ether or alcohol, but I cannot recommend the method, as by it a quantity of fatty oil is extracted, the subsequent separation of which is difficult, and occasions a loss of cantharidine.

Recapitulation.—Cantharidine exists in the insect in an uncombined state; and owing to the extractive matter present is taken up by water, in which menstruum when pure it is insoluble. To dry the watery extract readily, and obtain it in a fit state for exhaustion with alcohol, the charcoal is used. The ethereal extract will yield with alcohol a yellow (resinous) matter.

Properties.—Pure cantharidine forms white, glittering, odourless and tasteless scales. In water it is insoluble, and nearly so in cold alcohol, but readily in boiling alcohol; ether and fatty oils readily dissolve it in the cold. Heated it melts and volatilizes in white vapours, which possess in a marked degree the stupifying odour of Spanish flies, and condense on cold substances.

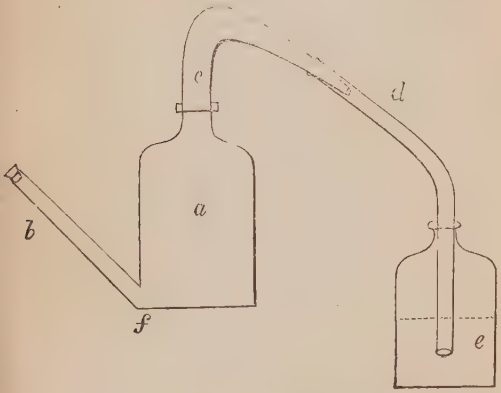
CARBON SULPHURATUM.

Carbonis Sulphidum.—Bi-Sulphuret of Carbon.

FORMULA: CS_2.

Preparation.—Sulphur in the form of vapour is passed over glowing charcoal, and the volatile product thus formed conducted into a receiver under water; the apparatus is thus arranged; (*a*) is a

vessel of fireproof clay or black lead, which is furnished with an earthenware tube (*b*), inclining sharply outwards, and well coated with clay at (*f*). This vessel filled with freshly heated pieces of charcoal about the size of a hazel nut is placed on the grate of a wind furnace. Upon it is luted an air-tight earthen head (*c*), the beak of which fits into a dip arm (*d*), whose lower end nearly reaches to the bottom of a glass receiver (*e*), half filled with water.



The head and tube (*d*) must be well luted together, but the mouth of the receiver is only loosely covered with a strip of bladder. The tube (*b*), which passes through the wall of the furnace, and serves to introduce the sulphur, is closed with an earthenware or cork stopper. As soon as the lutings are well dried, the fire is lighted, and when the vessel (*a*) acquires a red heat, the sulphur is introduced in single pieces of 4 or 5 drachms about every five minutes, the opening of the tube being again instantly closed

The evolution of gas commences instantly, and a heavy liquid condenses under the water in the receiver, which must be cooled with water, or better, ice or snow. The operation is terminated when sulphur five times the weight of the charcoal has been added. Whilst the apparatus cools, the tube (*b*) must remain open to prevent absorption of the liquid in (*e*). The preparation must undergo a rectification. The supernatant water is poured off as much as possible, and the residual heavy liquid distilled nearly to dryness at a gentle heat. A small portion is now shaken up with some carbonate of lead; if this be blackened, (and it is generally the case,) carbonate of lead is gradually added to the second distillate until a fresh portion does not acquire a brown colour, it is then allowed to subside, filtered, and the filtrate preserved in a well-closed bottle. The product is about as much as the sulphur employed. Metallic apparatus or tubes must be avoided in the manufacture of this substance, as they are readily acted on, and from the yield of sulphuret of carbon being diminished the loss is a double one.

Recapitulation.—Carbon and sulphur are without mutual action in the cold, but on sulphur being conducted in vapour over charcoal heated to redness, the two elements unite to a chemical compound:

1 at. C, and 2 at. S, form
1 at. CS_2.

75 Parts of carbon require 400 parts of sulphur, or 1 part of the former $5\frac{1}{3}$ sulphur; but the charcoal is not pure carbon, as it contains both hydrogen and inorganic constituents. For this reason a smaller proportion of sulphur would have sufficed, had it not been found in practice that during the passage of the sulphur vapours through the charcoal some portions escaped combination, and passing into the receiver remained dissolved by the sulphuret of carbon. The hydrogen of the charcoal also causes

the formation of sulphuretted hydrogen. To separate the dissolved sulphur the rectification is necessary, whilst carbonate of lead removes the sulphuretted hydrogen.

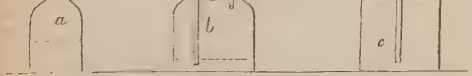
Properties.—Sulphuret of carbon is a colourless liquid, of a penetrating stinking smell somewhat similar to sulphuretted hydrogen, and a sharp pungent taste. Its spec. grav. is 1·26. In open vessels it volatilizes rapidly at the ordinary temperature, like ether. It has no action on vegetable colours. Water does not dissolve it; but in ether, alcohol, the fatty and ethereal oils, it is readily soluble. On evaporation it should yield no sulphur or fixed residue. If entirely volatile, but imparting a black colour to carbonate of lead, it is not free from *sulphuretted hydrogen.*

CHLORUM AQUOSUM.

Chlorine Water.

FORMULA: $Cl + xHO$.

Preparation.—At the present moderate price of hydrochloric acid, this is preferable to salt and sulphuric acid in the manufacture of chlorine. The apparatus is similar to that for generating sulphuretted hydrogen.



3 Parts hydrochloric acid spec. grav. 1·130 are poured with 1 part of water into the evolution flask (*a*), and water to the depth of ½ an inch into the

wash bottle (*b*), whilst 30 parts of distilled water are placed in (*c*). The two glass tubes are well fitted with corks into the tubulated wash bottle, luted and fastened with bladder, the bottle (*c*) arranged and only loosely covered at the mouth with a strip of bladder; both bottles are covered with black paper. To the acid in the evolution flask is now added 1 part of powdered peroxide of manganese, the opening of the bottle closed with a well-fitted cork in which is the short limb of a glass tube, and gently warmed. The evolution of gas instantly commences, and so soon as gas bubbles no longer appear in the bottle (*c*) it is removed, closed with a glass stopper, surrounded with dark paper, and kept in a cool place.

If the chlorine water is prepared in very cold weather, it is necessary to observe that the water in neither bottle reaches so low a temperature as + 50° Fah. otherwise the chlorine and water form a crystalline hydrate and stop up the tube.

Recapitulation.—When hydrochloric acid and peroxide of manganese = MnO_2 come in contact, the oxygen of the latter combining with the hydrogen of the acid forms water, one-half of the chlorine combines with the metal, forming protochloride of manganese, the other half is given off in the gaseous state. The water which is previously mixed with the acid and manganese, prevents the too rapid evolution of the gas:

1 at. MnO_2, and 2 at. HCl, form
2 at. HO, 1 at. MnCl, and 1 at. Cl.

545 Parts of pure peroxide of manganese require 910 parts of anhydrous hydrochloric acid, or 3500 parts spec. grav. 1·130 (= 26 per ct. anhydrous) for their entire decomposition. As however the native peroxide of manganese is never quite pure, and an excess is not of consequence, it is better as the cost is low to double the quantities, and instead of 545 parts use 1090, or 1 part to 3 parts of acid. The

chlorine evolved from 3 parts of hydrochloric acid having the above-named strength is sufficient to saturate 30 parts of water.

1 volume of water at the ordinary temperature absorbs 2 volumes of chlorine gas, and as 1 cubic inch of water at 62° Fah. weighs 252·45 grains, and 1 cubic inch of chlorine at the same temperature weighs 0·766 grains; so 30 fluid ounces of water (14400 grains) will require 2 volumes or 60 fluid ounces of chlorine ($87\frac{4}{10}$ grains) for its saturation; or 1 ounce will take up nearly 3 grains. In the 3 parts (ounces) of hydrochloric acid employed, there are 364 grains of chlorine, the half of which remains combined with the manganese as chloride. If the 182 grains of chlorine given off were entirely absorbed by water it would saturate 60 ounces, but experience shows that a portion passes through it and escapes absorption. If only half the above quantity of hydrochloric acid (that is, the stochiometrical quantity) be taken, a saturated chlorine water is not obtained, and thus the great excess of chlorine is necessary. In preparing large quantities of chlorine water, the unabsorbed chlorine is passed through milk of lime to get rid of it and prevent any disagreeable effects from it. By washing in the bottle (*b*) traces of manganese and hydrochloric acid, which may be carried over, are retained. By surrounding the bottle with paper, the action of daylight is prevented, which decomposes the water forming hydrochloric acid, oxygen being evolved; (the direct sunlight is a still more powerful agent).

1 at. Cl, and 1 at. HO, form
1 at. ClH, and 1 at. O.

The conversion of chlorine water into hydrochloric acid goes on, though more slowly, even under the exclusion of the daylight, and for this reason chlorine water must not be kept too long, not more than two months.

The residue from the preparation of chlorine is applicable for chloride of manganese. The excess of peroxide of manganese is washed, dried, and reserved for a second treatment with hydrochloric acid.

Properties.—Well saturated chlorine water is a clear, greenish-yellow liquid of a peculiarly choking smell, and feeble styptic taste. It bleaches litmus paper instantly. In the daylight, and more rapidly in the direct sunlight, it becomes colourless under the formation of hydrochloric acid and free oxygen, (*vide supra*);* so soon as all the free chlorine is gone, litmus paper, instead of being bleached, is only reddened by it. Chlorine water, which has lost its colour, and smells but faintly of the gas, is inapplicable to medical purposes. The formation of hydrochloric acid commences with the preparation of chlorine water, but so long as the quantity of chlorine preponderates over that of hydrochloric acid in the solution, litmus paper will be bleached by it. To determine the presence of hydrochloric acid, agitate for half an hour with excess of metallic mercury, or until all smell of chlorine has disappeared; if after filtration litmus paper is reddened, the presence of hydrochloric acid is evident; but should the colour not be affected, nitrate of silver will cause an opalescence if it contain the smallest trace of hydrochloric acid. The chlorine combining with the mercury forms calomel = Hg_2Cl, which is insoluble, whilst the hydrochloric acid has no action on the metal. By previously weighing the quicksilver, the loss of weight sustained will give the quantity of chlorine in the water. Freshly prepared chlorine water, as already stated, contains about three grains in an ounce.

* We may assume that the first portion of free oxygen forms with the chlorine present, hypochlorous acid, ClO, which by further action of the light and water is converted into hydrochloric acid and free oxygen.

COBALTUM OXIDATUM NITRICUM.

Cobalti Nitras.—Nitrate of Cobalt.

FORMULA: $CoO + NO_5 + 2HO$.

Preparation.—Commercially pure Saxon oxide of cobalt, but which always contains a little arsenic and nickel, is digested for two days with six times its weight of pure nitric acid, spec. grav. 1·20, in glass flask, in a sand bath, and filtered. If, as is generally the case, a portion remains undissolved, it is washed, dried, and reserved for another occasion. The acid solution is evaporated in a porcelain dish until a small portion gives signs of crystallization; the dish is then placed in a sand bath, and warmed with constant stirring, so long as nitric acid vapours are given off, and until the solution becomes a dry powder, which is to be kept in a well-closed bottle. 3 Parts of black oxide yield $6\frac{3}{4}$ parts of dry (anhydrous) salt.

To obtain the salt crystallized, it is dissolved with a gentle heat in half its weight of pure distilled water, and the solution slowly evaporated in a sand bath. Instead of $6\frac{3}{4}$, the salt now equals 8 parts (being in combination with 2 at. of water).

Recapitulation.—The black oxide of cobalt met with in commerce, and marked, if Saxon, R.K.O., contains rather more oxygen than the oxide, 6 at. of cobalt and 7 of oxygen $= C_6O_7$. Nitric acid acts on it but slowly, and only by continued digestion entirely dissolves it; nitrate of oxide of cobalt is formed, and oxygen evolved:

1 at. C_6O_7, and 6 at. NO_5, form
6 at. $CoO + NO_5$, and 1 at. O.

2914 Parts of the black oxide require 4050 parts of anhydrous nitric acid, or 15000 parts of acid of spec. grav. 1·20 (73 per ct. of water). In these proportions (1 part of oxide and 5 of hydrated acid) a

small portion of the former will always remain undissolved, consequently when an entire solution is required, the acid must be increased by 1 or 2 parts. In evaporating the solution to dryness, great care must be taken, especially towards the end of the operation, that the temperature does not become too high, and it must be moderated by constant stirring, otherwise after the evaporation of the free nitric acid, a portion of the nitrate becomes decomposed into free nitric acid and a basic salt, the base of which by further action of the heat is converted into peroxide of cobalt = Co_2O_3, and the acid robbed of one atom of oxygen escapes. When this partial decomposition has occurred, a gray residue occurs on treating with water, consisting of basic salt and peroxide. The anhydrous and crystallized salt both attract moisture from the air with avidity, and deliquesce.

Properties.—Pure nitrate of cobalt forms either a violet powder or small pink prisms, smelling faintly of nitric acid, and having a pungent and astringent taste; it deliquesces in the air, and dissolves very readily in water and alcohol; the solutions have an acid reaction. After adding a few drops of hydrochloric acid to the aqueous solution, sulphuretted hydrogen, even on standing some days, must cause no change in it. Should a yellow precipitate ensue, it is from *arsenic* or *arsenious acid*; if dark coloured, *copper* may be present. If, after the addition of sal ammoniac to the solution of the nitrate, excess of solution of ammoniac, instead of entirely dissolving it, leaves a brown precipitate, it shows the presence of *iron*; the sal ammoniac forms a double salt, not decomposed by ammonia, otherwise a portion of the oxide of cobalt would be thrown down as a green basic salt that does not readily dissolve again. Under the same circumstances an apple green precipitate with caustic potash will arise from *nickel*, the double salt of cobalt and ammonia not

being decomposed by potash in the cold, whilst that of nickel is. If copper and iron are present, the oxide of nickel cannot be with certainty determined until these are removed, the first by sulphuretted hydrogen, the last by ammonia, as both these metals are thrown down by caustic potash.

COLLODIUM.

Collodion.

Preparation.—30 Parts of concentrated sulphuric acid, and 20 parts of powdered nitrate of potash, are placed in a glass cylinder, well stirred with a glass rod, and 1 part of clean and lightly-compressed cotton wool that has previously been well dried added; after being allowed to remain not more than five minutes, it is withdrawn and thrown into a dish of cold water, well washed several times with fresh water, spread out on a glass plate, and dried at the ordinary temperature. The dried preparation (named, from its explosive properties, Gun Cotton) is pulled and cut as finely as possible, then placed in a bottle with thirty times its weight of ordinary ether, and thoroughly shaken for some minutes, allowed to digest with occasional shaking for some hours, strained through thick linen, and the clear solution kept in well-stopped bottles.

Only carefully-prepared gun cotton must be used for collodion, and that which, having undergone no change, does not redden moistened litmus paper.

Recapitulation.—As explained under the article Acid. Nitric. there are formed by the action of sulphuric acid on nitre, bisulphate of potash and free nitric acid. For the entire decomposition of the nitre in the warm its weight of sulphuric acid is necessary; the above method gives half as much again sulphuric acid, which partly compensates

for the want of artificial heat, and also insures the nitric acid in the most concentrated form. Of course this last acid may be obtained by mixing the strongest nitric acid with a third, half, or equal volume of concentrated sulphuric acid, but I prefer the nitre, as producing a cotton of greater solubility in ether. To obtain good results the above method must be strictly followed; the cotton immersed in the mixture of nitre and sulphuric acid just made (and still warm), and not allowed to remain in it more than five minutes, otherwise it acquires a yellow colour, loses its looseness of texture, and is only partially soluble in ether. The change which the cotton wool ($C_{12}H_{10}O_{10}$) undergoes by the action of the nitric acid is to lose the elements of 3 at. of water, which are replaced by 3 at. of nitric acid:

1 at. $C_{12}H_{10}O_{10}$, and 3 at. NO_5, form
1 at. $C_{12}H_7N_3O_{22} = C_{12}H_7O_7 + 3\,NO_5$, and 3 at. HO.

2025 Parts of cotton wool should give 3713 parts of gun cotton, but somewhat less than this is obtained, as some portion of the cotton wool almost always remains unacted on. The gun cotton experiences an incipient decomposition when gently warmed, increasing with the temperature to 268° Fah., when it explodes. The drying, consequently, must take place only at the ordinary temperature, but even then after some time the gun cotton undergoes a change, acquiring the smell and acid reaction of nitric acid, becoming, according to the extent of the decomposition, less and less soluble in ether. It is better to use that recently prepared for collodion. Ether dissolves the pure product entirely, leaving the cotton wool behind, consequently the solution never has a bright appearance; most of the cotton is removed by straining, the remainder deposits on standing; when strained it is clear enough for all ordinary purposes.

Properties.—Collodion is a colourless, thickish

liquid, having a neutral reaction, and when spread on any surface quickly forming a thin transparent adhesive pellicle, unacted on by air or water, and is therefore applicable to many surgical purposes and in the arts. Collodion prepared from gun cotton slightly decomposed has an acid reaction, and yields an opaque residue, which is not adhesive, and consequently useless.

CUPRUM OXIDATUM.

Cupri Oxidum.—Oxide of Copper.

FORMULA: CuO.

Preparation.—(a) From Basic Carbonate of Copper.—A portion of this salt is tightly pressed into a Hessian crucible, the latter covered and heated, at first gently, and then to redness, for half an hour. Before it is quite cold, the powder is removed, and placed in a well-stopped bottle. 3 Parts of carbonate yield 2 parts.

(b) From Nitrate of Copper.—An earthenware crucible is heated to redness, and dried nitrate of copper thrown into it by small spoonfuls at a time, with the precaution of waiting before adding a fresh portion, until the previous quantity is decomposed; when the whole is in the crucible heat to redness for half an hour, and bring the heavy black powder whilst warm into a well-closed bottle. 5 Parts of nitrate of copper give 2 parts of oxide.

Recapitulation (a).—The basic carbonate of copper ($CuO + CO_2$, $CuO + HO$) loses its carbonic acid and water by heating, leaving pure oxide of copper. *(b)* The dry nitrate of copper also allows its acid to escape, which for want of water is at the moment of its liberation decomposed into hyponitric acid ($=NO_4$) and oxygen, consequently the vapours from the crucible are not colourless, but

brownish yellow. As the oxide of copper readily attracts moisture, it must whilst still warm be excluded from the atmosphere.

Properties.—Oxide of copper is a black powder, which, prepared by the process (*a*), is light, but that from (*b*) heavy and compact. It has neither smell nor taste. In acids it is readily soluble, forming green or blue solutions, rendered deep blue by excess of ammonia; by a small quantity of ammonia a greenish precipitate is certainly formed, but it disappears on adding more of the precipitant. The theory of this behaviour with ammonia, as generally accepted, is that the ammonia takes the acid from the oxide of copper, with which the ammoniacal salt thus formed combines, all being precipitated together, but this precipitate is dissolved on the addition of more ammonia, which, combining with it, forms a soluble salt—for instance:—

1 at. $CuO + NO_5$, and 1 at. NH_3, form
1 at. $NH_3 + CuO + NO_5$ as a green precipitate, and this with
1 at. NH_3, and 1 at. HO, forms
1 at. $NH_4O + NO_5$, $NH_3 + CuO$.

If on treating the oxide of copper solution with excess of ammonia, there is a brown flocculent residue, it results from *peroxide of iron*.

CUPRUM OXIDATUM ACETICUM.

Cupri Acetas.—Ærugo depurata, seu Crystallizata.—Neutral Acetate of Copper.

FORMULA: $CuO + \bar{A} + HO$.

Preparation.—1 Part of ordinary verdigris is rubbed with 6 parts of distilled water, the mixture heated in a porcelain dish, and with constant

stirring concentrated acetic acid is added until the whole is dissolved (1 part of acid spec. grav. 1·045), filtered whilst hot, and the filtrate placed in a cool spot for crystallization. After some days the mother liquor is separated, and evaporated to crystallization repeatedly, so long as it contains any salt. The crystals are collected, spread on filtering paper, dried at the ordinary temperature, and kept in a closed bottle. They weigh rather more than the verdigris used.

Recapitulation. — Verdigris is a basic acetate of oxide of copper, having the composition $2CuO + \bar{A} + 6HO$. It requires another atom of acid for its conversion into a neutral salt entirely soluble in water, of which 2 eq. are then formed.

1 at. $2\,CuO + \bar{A} + 6\,HO$, and 1 at. A, form
2 at. $CuO + \bar{A} + HO$, and 4 at. HO.

2305 Parts of verdigris require, according to theory, only 1772 parts of acetic acid, spec. grav. 1·045 (=64 per ct. water); a slight excess of acid is however necessary, otherwise the salt will not dissolve; the impurities mechanically mixed with verdigris, as grape skins, wood, &c., remain behind on the filter.

Properties.—Neutral acetate of copper forms dark green rhombic prisms, having a feeble smell of acetic acid, and nauseous metallic taste; it effervesces in the air, becoming coated with a pale green powder. Water at the ordinary temperature dissolves $\frac{1}{13}$, and boiling $\frac{1}{5}$ of the salt. Alcohol, with greater difficulty, dissolves it also. It must form a perfectly clear solution with carbonate of ammonia.

CUPRUM OXIDATUM CARBONICUM BASICUM.

Cupri Subcarbonas.—Basic Carbonate of Copper.

FORMULA :

$$2CuO + CO_2 + HO = CuO + CO_2,\ CuO + HO.$$

Preparation.—1 Part of sulphate of copper is dissolved in 10 parts of pure water, and a solution of carbonate of soda, in three times its quantity of water, is added so long as it causes a precipitate (rather more than 1 part of crystallized soda will be found necessary); this is allowed to deposit, thrown on a filter, washed thoroughly with water, and dried with a gentle heat. The yield is not quite half that of the sulphate used.

Recapitulation.—When carbonate of soda solution comes in contact with one of sulphate of copper, it takes from the latter its sulphuric acid, whilst the oxide of copper, combining with half the liberated carbonic acid, is thrown down as a basic carbonate of copper:

2 at. $CuO + SO_3 + 5HO$, and 2 at. $NaO + CO_2 + 10HO$, form
1 at. $2CuO + CO_2 + HO$, 2 at. $NaO + SO_3$, 1 at. CO_2, and 29 at. HO.

3118 Parts of sulphate of copper require 3580 parts of soda.

Properties.—Basic carbonate of copper is a clear green light powder, odourless and tasteless, dissolving in acids with effervescence, and being soluble in caustic ammonia. Heated to redness, it is reduced to pure oxide of copper. Water boiled in it must give no precipitate with chloride of barium, otherwise *sulphate of soda* is present. Any *iron* that may be present is known, as with oxide

of copper, by the brown residue on treating with caustic ammonia; if the common commercial sulphate of copper has been used, zinc may be present. To determine this, dissolve the powder in nitric acid, decompose the solution with excess of caustic potash, filter and add to the filtrate a few drops of hydrosulphuret of ammonia; if this causes a white precipitate *zinc* is present. Oxides of copper and iron are entirely thrown down from the solution of the nitrate by caustic potash, whilst excess of this holds oxide of zinc in solution; but hydrosulphuret of ammonia causes the precipitation of the latter with the formation of white sulphuret of zinc, sulphuret of potassium, and free ammonia, which have not the power of dissolving sulphuret of zinc.

CUPRUM OXIDATUM NITRICUM.

Cupri Nitras.—Nitrate of Copper.

Formula of the Dried Salt: $CuO + NO_5$.
Formula of the Crystallized: $CuO + NO_5 + 3HO$.

Preparation.—Small pieces of metallic copper or copper scales are added to nitric acid, spec. grav. 1·20, in a capacious glass flask, until the metal is no longer acted on (8 parts of acid of this strength dissolve 1 part of metal; 7 parts of acid, 1 part of copper scales); the flask is then placed in a sand bath, and warmed to dissolve the last portion of acid; the solution is allowed to settle, then decanted, filtered, and evaporated with constant stirring in a porcelain dish, at first over a naked fire, and afterwards, when the mass becomes pasty, on a sand bath to dryness. The dried powder is instantly placed in a well-closed bottle.

If the salt is required crystallized, the powder i

dissolved in half its weight of pure water, in the sand or water bath. The crystals separating in the cold must be quickly dried between paper, and kept from contact of the air.

1 Part of metal forms 3 parts of dry and nearly 4 parts of crystallized salt. From 1 part of copper scales rather less is obtained.

Recapitulation.—When metallic copper and nitric acid come in contact, there is even in the cold a lively action, and the copper is dissolved; 1 at. of nitric acid gives up 3 at. of oxygen to 3 at. of copper; the oxide of copper thus formed combines with 3 at. nitric acid to nitrate of copper, whilst the nitric acid, deprived of its 3 at. of oxygen, is given off as nitric oxide $= NO_2$, and coming in contact with the air acquires 2 at. of oxygen, forming brownish-yellow vapours of hyponitric acid $= NO_4$.

3 at. Cu, and 4 at. NO_5, form
3 at. $CuO + NO_5$, and 1 at. NO_2; the latter with 2 at. $O = O_4$.

1188 Parts of copper require 2700 parts of anhydrous nitric acid, or 10000 parts of spec. grav. 1·20 (containing 27 per ct. of anhydrous acid). In using copper scales, which are principally protoxide of copper, a saving of acid is effected. We then have from

3 at. Cu_2O, and 7 at. NO_5,
6 at. $CuO + NO_5$, and 1 at. NO_2.

Or, 2676 parts of protoxide require 4725 parts of anhydrous nitric acid.

The evaporation of the salt must towards the end be most carefully conducted, as the combination of nitric acid with oxide of copper is not very stable, and even in the sand bath may be converted into free acid and a basic salt, if too high a temperature is not prevented in any portion of the salt by constant stirring.

Properties.—Nitrate of copper forms either a pale blue crystalline powder or deep blue rhombic prisms, smelling faintly of nitric acid, and of a nauseous pungent metallic taste and acid reaction. It deliquesces in the air; water and alcohol both dissolve it. Heated in a platinum spoon it fuses, giving off water and nitric acid, and leaving a clear green basic salt $= 5CuO + NO_5$, which still further heated becomes pure oxide of copper. *Oxide of iron*, with which, from the copper, it is generally contaminated, may be detected as in the foregoing preparations.

CUPRUM OXIDATUM SULPHURICUM.

Cupri Sulphas.—Sulphate of Copper.—Blue Vitriol.

FORMULA: $CuO + SO_3 + 5HO$.

Preparation.—2 Parts of metallic copper in small pieces, $3\frac{1}{3}$ of concentrated sulphuric acid, 12 parts of water, and 4 parts of nitric acid, spec. grav. 1·20, are put into a glass flask, and the latter placed in a sand bath, heated, at first gently, and afterwards boiling, as long as there is any perceptible action on the copper; it is then filtered, and placed in a cool spot. The salt which separates after some days is collected, the mother liquor evaporated so long as crystals will form; these are spread on a piece of filtering paper to dry in the air. The produce will be 7 parts of blue vitriol for 2 of copper.

In this case, instead of metallic copper, the copper scales will be more economical to use; the relative proportions in this case, substituting 2 parts of nitric acid for 4, will remain the same.

Recapitulation.—Metallic copper is scarcely acted on by dilute sulphuric acid, even when warmed;

the addition of sufficient nitric acid to oxidize it causes it readily to dissolve. The nitric oxide from the reduced nitric acid is evolved, and forms the brown vapours of hyponitric acid:

3 at. Cu, 3 at. SO_3, and 1 at. NO_5, form
3 at. $CuO + SO_3$, and 1 at. NO_2.

1188 Parts of copper require 1839 parts of hydrated sulphuric acid, and 2500 parts of nitric acid spec. grav. 1·20 (27 per ct. anhydrous acid); the remainder of the process requires no explanation. By using copper (forge) scales less nitric acid is requisite, as they consist principally of suboxide of copper = Cu_2O, which already contains the half of the necessary oxygen.

On the small scale sulphate of copper is generally prepared by boiling small portions of copper with concentrated sulphuric acid, one portion of which yields one atom of oxygen to the copper, and passes off as sulphurous acid; the oxide of copper thus formed combines with another portion of the sulphurous acid:

1 at. Cu, and 2 at. SO_3, form
1 at. $CuO + SO_3$, and 1 at. SO_2.

396 Parts of copper require 1226 of concentrated sulphuric acid. This is more than is indicated by theory, but during the process a portion of the acid volatilizes undecomposed, and even with a very large excess the solution always contains, besides sulphate of copper, some portions of the metal more or less oxidized. This process is only to be recommended in cases where the sulphurous acid can be employed, as in bleaching, &c.*

Properties.—Sulphate of copper forms deep blue transparent oblique rhombic crystals, is odourless, and possesses an astringent nauseous metallic taste.

* Or the formation of sulphites.—Ed.

Exposed to the air it gradually gives off water and acquires a white coating. Heated it fuses, losing its water and forming a white mass, which at a red heat also gives off its acid, yielding oxide of copper. It dissolves in 3½ cold, an equal weight of hot water and is insoluble in alcohol. Its solution has an acid reaction. The ordinary blue vitriol prepared from native sulphuret of copper contains several impurities, especially *oxide of iron* and *oxide of zinc;* the detection of these is described under CUPRUM CARBONICUM.

CUPRUM OXIDATUM SULPHURICUM AMMONIATUM.

Cupri Ammonio Sulphas.—Ammoniated Sulphate of Copper.

FORMULA: $(NH_4O + SO_3) + (NH_3 + CuO)$.

Preparation.—Sulphate of copper is finely powdered in a porcelain mortar, and liquor ammonia added until the salt is dissolved. 1 Part of blue vitriol requires about 3 parts of ammonia spec. grav. 0·960. The solution is poured into a glass cylinder containing twice its weight of alcohol of 80 per ct.; the liquids are well mixed, the blue crystalline powder allowed to subside, collected on a linen cloth, pressed, and spread on filtering paper to dry; the paper must be renewed as long as it becomes damp, and when the salt is thoroughly dry it is to be kept in a well-closed bottle. The weight of the product will be about that of the sulphate of copper used. If desired in large crystals, the ammoniacal solution is first introduced into the cylinder, then the alcohol, taking care that the two liquids do not become mixed; the vessel is tied over with bladder, and allowed to remain for some weeks in a

cool place. The salt is then collected and dried as in the preceding method.

Recapitulation.—In order the more readily to understand the process, we will suppose the sulphate of copper to be dissolved in water; in this solution ammonia added by drops causes a greenish precipitate, which however is soluble in an excess of the precipitant, to a deep blue liquid. The green precipitate is thus formed:—1 at. of anhydrous sulphate of copper combines with 1 atom of ammonia to $NH_3 + CuO + SO_3$. By solution in ammonia an atom of the latter and 1 atom of water combine with it, and it may now be considered as a compound of sulphate of ammonia and ammoniated oxide of copper, $= (NH_4O + SO_3) + (NH_3 + CuO)$. Or, as when moderately heated only neutral sulphate of copper remains, the salt may be assumed to be a compound of 2 at. of ammonia, 1 at. of sulphate of copper, and 1 at. of water, $= 2NH_3 + (CuO + SO_3) + HO$. To obtain this salt, 1 at. of sulphate of oxide of copper, or 1559 parts of crystallized sulphate of copper ($CuO + SO_3 + 5HO$) and 2 at. of ammonia, or 4260 parts of liquor ammonia spec. grav. 0·960, containing 10 per ct. of anhydrous ammonia, are requisite. It cannot be obtained by evaporating, the solution being decomposed and losing 1 at. of ammonia. The supernatant liquid contains but a small portion of the salt. When the alcohol is quickly mixed with the solution the salt falls as a crystalline powder; but if allowed to do so slowly, the water is gradually abstracted and the salt forms long flat prisms. On account of its readiness to decompose in the air it must be dried as quickly as possible without the application of heat, and kept in a well-closed bottle.

After saturating the ammoniacal solution with sulphuric acid, the alcohol may be re-obtained by distillation.

Properties.—The ammoniacal sulphate of ammonia forms either a deep blue crystalline powder, or simi-

larly coloured long flat prisms and needles, having an ammoniacal odour, and a nauseous metallic taste. It must entirely dissolve in $1\frac{1}{2}$ parts of cold water; but in a large quantity of water it becomes decomposed, a pale blue powder precipitating which contains less ammonia. It undergoes the same change in the air, but if exposed to it for a great length of time, gives off one entire atom of ammonia (and 1 at. water), leaving the previously mentioned green compound, $NH_3 + CuO + SO_3$, which carefully warmed loses the second atom of ammonia, a white residual powder, neutral sulphate of copper, remaining.

CUPRUM SUB-OXIDATUM.

Cupri Suboxidum.—Sub-Oxide of Copper.

FORMULA: Cu_2O.

Preparation.—(*a*) *By the dry way.*—A number of moderately thick copper plates about 2 inches square are piled, not too thickly, on each other in an earthen crucible, heated to redness and withdrawn about every ten minutes; the crust formed on them is readily removed with a knife, and the plates again heated; this may be repeated until they are as thin as paper, when there is danger in removing the oxide of contaminating it with pieces of metallic copper. The reddish gray scales are rubbed to a fine powder and kept in a closed bottle.

(*b*) *By the moist way.*—1 Part of sulphate of copper and 1 part of sugar of milk are dissolved in 10 parts of water in a porcelain dish, and solution of caustic potash added until the greenish precipitate at first formed entirely dissolves (3 parts of solution spec. grav. 1·333 will suffice); the dish is placed in a water

bath and heated with continuous stirring. The clear deep blue liquid, even before the water boils, acquires a greenish-gray colour, becomes turbid and of a brown colour, then of a clearer yellow, and finally almost a cinnabar red; the dish is now at once removed, the contents poured into a large quantity of cold water, the precipitate separated from the supernatant yellow liquid, washed and dried. If the heating is continued too long the clear red (amorphous) precipitate becomes crystalline and of a dark cochineal red. The dish cannot be heated higher than this without injuring the preparation, which becomes further oxidized and acquires a blackish appearance.

From 7 parts of crystallized sulphate of copper, 2 parts of suboxide are obtained.

Recapitulation. — (*a*) Metallic copper heated to redness in the presence of air combines with the oxygen, forming suboxide. The outer portion of the latter however becomes instantly covered with a thin layer of oxide, which protects that below from further action of the oxygen. That portion of the copper which has combined with oxygen may be readily separated from the unoxidized part; it forms crystalline plates or leaves, which rubbed up form a grayish cochineal red powder. When the metal is repeatedly heated, a considerable quantity of the suboxide of copper may soon be formed, certainly not perfectly free from oxide, but applicable to most technical purposes, as colouring glass red, &c. The proportion of oxide is generally about $\frac{1}{20}$.

(*b*) When caustic potash is added to a solution of sulphate of copper, a clear green precipitate of basic sulphate of copper is first caused, 2 at. of potash abstracting 2 at. of acid from 3 at. of sulphate of copper, forming 2 at. neutral sulphate of potash.

2 at. KO, and 3 at. $CuO + SO_3 + 5HO$, form
2 at. $KO + SO_3$, 1 at. $3CuO + SO_3 + 3HO$, and
12 at. HO.

On a further addition of potash, the above precipitate is converted into clear blue hydrated oxide of copper, which is not dissolved even by a great excess of potash, its sulphuric acid passing to the potash.

1 at. KO, and 1 at. $3CuO + SO_3 + 3HO$, form
1 at. $KO + SO_3$, and 3 at. $CuO + HO$.

If, however, the solution contains a certain portion of sugar of milk, instead of there being formed a permanent precipitate of oxide of copper, the latter is instantly and entirely dissolved to a deep blue liquid, a cuprate of potash being formed; 3 at. of oxide of copper require for this purpose 3 at. of potash, and about $2\frac{1}{4}$ at. of crystallized sugar of milk ($C_{12}H_{10}O_{10}$).

3 At. of sulphate of copper = 4677 parts, $2\frac{1}{4}$ at. of sugar of milk = 4556 parts, and 6 at. anhydrous potash = 3540 parts, or 13615 parts of solution of caustic potash, of spec. grav. 1·333 (containing about 26 per ct. of anhydrous potash). The potash must always be slightly in excess, consequently the proportions of sulphate of copper, milk sugar, and potash, given in the process, are the correct ones.

The combination of oxide of copper and potash becomes decomposed in the warm, owing to the action of the milk sugar, the oxide of copper yields half its oxygen to the elements of the milk sugar, and being reduced to a suboxide forms a yellow hydrated precipitate, which however quickly loses its water of hydration and assumes a red colour. The reaction occurs perfectly quietly, without effervescence. The object of rapidly cooling the precipitate is to preserve its fine red colour. The supernatant liquor, which immediately after the precipitation is colourless, quickly becomes yellow; it does not, however, contain a particle of copper dissolved. The most important product of oxidation of the milk sugar is formic acid, which is formed in a similar manner as in the action of

peroxide of manganese on sugar; (*vide* ACIDUM FORMICUM).

Properties.—Suboxide of copper is an odourless and tasteless powder; in its amorphous state it is a clear copper colour, or approaching that of red lead; crystallized, a dark cochineal red. Treated with hydrochloric acid it acquires a white colour, and readily dissolves, on warming, to a pale green liquid; the white colour arises from the formation of subchloride of copper.

1 at. Cu_2O, and 1 at. HCl, form
1 at. Cu_2Cl, and 1 at. HO,

which should in reality be colourless; but the affinity of the substance for chlorine is so great as to cause it to decompose a portion of the hydrochloric acid in excess, and combine with the chlorine, which gives the solution a green appearance. If the preparation has a dirty gray or blackish colour, it contains oxide.

DIGITALINUM.

Digitaline.

FORMULA: ?

Preparation.—A quantity of the coarsely-powdered leaves of the digitalis purpurea are digested with eight times their weight of alcohol, of 80 per ct., at the ordinary temperature, for some days, the residue pressed and washed with a little alcohol, filtered, and most of the spirit distilled from it, the contents of the retort evaporated to the consistence of an ordinary extract, and treated with a mixture of 1 part of concentrated acetic acid and 30 parts of water, in a water bath. The acetic acid solution is agitated with animal charcoal that has been purified by digestion with hydrochloric acid; then filtered,

neutralized with ammonia, and precipitated with an aqueous solution of tannin, the precipitate collected on a filter, exhausted with water, rubbed with about $\frac{1}{6}$ its weight of finely-powdered oxide of lead, and dried in a water bath. The dried mass is finely powdered, exhausted with alcohol 90 per ct., and filtered; the filtrate treated with animal charcoal, and slowly evaporated in a water bath.

When all the alcohol is removed, and the residue becomes nearly dry, it is rinsed a few times with pure water, thoroughly dried, shaken with ether, the ether poured off, and the residue dissolved in warm alcohol, of 90 per ct., then slowly evaporated. The yield is about $\frac{1}{70}$ or $\frac{1}{80}$ the weight of the dried leaves used.

Recapitulation.—To obtain a good yield and pure digitaline, it is necessary to employ as small an amount of heat as possible. Alcohol readily dissolves digitaline at the ordinary temperature, but at the same time takes up extractive matter, &c., which gives the tincture a dark colour. Acetic acid dissolves from the alcoholic extract all the digitaline, and but a part of the colouring matter, which last is almost entirely removed by animal charcoal. After the acetic acid has been neutralized by ammonia, tannin precipitates the digitaline, and in order to free it from the precipitant, the latter is combined with oxide of lead, with which it forms an insoluble compound. From the residual extract of the alcoholic solution, water takes up only a trace of extractive matter; ether, some other impurities, with only a trace of digitaline. After dissolving in alcohol, and allowing this to evaporate very slowly, the digitaline is obtained quite pure.

Properties.—Pure digitaline forms white, odourless, warty masses, of a persistent bitter taste, which is but slowly perceptible from its insolubility. Its dust excites violent sneezing. When heated

gradually, it first melts, evolves acid vapours, ignites, and finally is consumed without residue. It is soluble in 2000 parts of cold and 1000 of hot water; in 288 parts of ether, spec. grav. 0·750, and 1250 parts of ether, 0·726; it is readily soluble in alcohol, the more so the stronger and warmer the latter is. All these solutions have a neutral reaction. Acetic acid readily dissolves the digitaline, which, however, combines neither with this nor any other acid, but behaves as a nitrogenous chemically indifferent substance. Mineral acids have a destructive action on it, more or less; concentrated hydrochloric acid rapidly dissolves it to a yellow liquid, which becomes emerald green, and gradually of a deep green, whilst, finally, green flakes are deposited; concentrated sulphuric acid gives a blackish-brown solution, which after several days becomes brownish red, amethyst gray, finally cochineal red, and on diluting with water acquires a green appearance. Ammonia does not appear to affect it; but with potash it gradually loses its bitter taste.

ERGOTINUM OFFICINALE.

Officinal Ergotine.

Preparation.—Coarsely-powdered ergot of rye is digested, at the ordinary temperature, with eight times its weight of cold water, for some days, filtered, pressed, and the residue washed once or twice with water, the clear liquid heated to boiling, filtered when cold, and evaporated in a water bath to a syrupy consistence. The syrup is agitated with eight times its weight of alcohol, of 80 per ct., filtered, the alcohol distilled off at a very low temperature, and the contents of the retort slowly evaporated, in a water bath, to the consistence of an ordinary extract.

Recapitulation.—By treating the ordinary extract with alcohol, all the gummy matters contained in it, and which have no effect, are removed.

Properties.—The ergotine, as above prepared, is a clear dark brown extract, of an agreeable odour, resembling roasted meat, and of a pungent bitter taste, like decomposing corn. In water and alcohol it forms a reddish-brown solution.*

FERRUM BROMATUM.

Ferri Bromidum.—Bromide of Iron.

FORMULA: $FeBr + 2HO$.

Preparation.—2 Parts of bromine and 2 of water are placed in a flask, 1 part of iron filings added gradually, and thoroughly agitated. When no more action occurs, and the brown colour of the fluid is exchanged for green, the liquid is filtered from the excess of iron and carbon which has separated, and evaporated in a clean iron dish, or the sand bath, to dryness, constantly stirring, and the salt quickly transferred to a well-closed bottle. Its weight is from 3 to 3½ parts.

Recapitulation.—Bromine combines directly with iron; the water which floats on the bromine prevents a large quantity of the latter from escaping during the evolution of heat; to prevent the action from being too violent, the iron is added gradually.

1 at. Br, and 1 at. Fe, form
1 at. FeBr.

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* From a number of well-directed experiments, M. Bonjean, pharmacien, of Geneva, has come to the conclusion that the active principles of ergot are of two different characters; the one, soluble in ether, being intensely poisonous, whilst the one exerting an action on the uterus is insoluble in ether, but dissolves in cold water. That prepared as directed in this work, he states to be without any action. We strongly recommend a perusal of M. Bonjean's interesting pamphlet.—ED.

1000 Parts of bromine consequently require only 350 of iron, but an excess of the latter is of no consequence. The solution absorbs oxygen from the air with great avidity, forming oxide of iron with a portion of the iron; the bromine thus liberated unites with another portion of the protobromide of iron, and forms perbromide.

The most rapid evaporation in an iron dish will not entirely prevent this, but limits it to a small portion. When the mass begins to thicken it must frequently be removed from the fire, to try whether it hardens on cooling, and as soon as this happens it is to be transferred to a well-closed bottle.

Properties.—Evaporated to dryness (it still contains 2 at. of water) bromide of iron forms a grayish-white or greenish-yellow crystalline powder, is odourless, and tastes at first pungently saline, afterwards sweetly astringent; in the air it deliquesces and oxidizes (*vide supra*). In water and alcohol it is readily soluble, the oxidized portions being left behind; the solutions have an acid reaction. In its chemical and physical properties it assimilates to the chloride of iron, but differs from it in this respect, that when the iron has been precipitated by caustic potash, the supernatant liquid (bromide of potassium) acquires, on the addition of chlorine water, a reddish colour, whilst that from protochloride of iron, similarly treated, would become at most only a light greenish yellow. Chlorine separating the bromine from the bromide of iron, replaces it, and the free bromine remains dissolved as such. By this method, an adulteration with chloride of iron is not to be detected; for this I must refer to the article HYDRARGYRUM BROMATUM.

FERRUM CHLORATUM.

Ferri Chloridum.—Protochloride of Iron.

FORMULA OF THE DRIED: $FeCl + 2HO$.
FORMULA OF THE CRYSTALLIZED: $FeCl + 4HO$.

Preparation.—4 Parts of hydrochloric acid, spec. grav. 1·130, are mixed, in a roomy glass flask, with 1 part of iron (in filings or turnings); when the first violence of the action is over, the flask is digested in the sand bath as long as evolution of gas occurs, and the liquid filtered. The clear deep green solution, after the addition of $\frac{1}{4}$ part of hydrochloric acid, is evaporated, at first over a naked fire in a retort, and, when reduced to about $\frac{1}{3}$, in a porcelain dish on a sand bath, at a gentle heat and with constant stirring, to dryness; the crystalline powder, whilst still warm, is placed in a well-closed bottle. It will weigh about $2\frac{3}{4}$ parts. If required in crystals, the evaporation must not be long continued, the liquid then transferred to a cylinder covered with bladder, and placed in the cool. The green crystals which separate are quickly dried between filtering paper, and kept carefully excluded from air and moisture.

Recapitulation.—Metallic iron is rapidly acted on and dissolved by hydrated hydrochloric acid; in order that the evolution of gas be not too rapid, the iron is added to the acid gradually, or *vice versâ*. The chlorine of the acid combines with iron, and forms protochloride, the hydrogen of the acid is evolved. The gas thus set free possesses a disagreeable smell, from the presence of light carburetted hydrogen $= CH_2$, which is formed at the expense of the carbon, from which even the best iron is not entirely free. The carbon is present in the iron partly in combination, partly as a mixture; it is the

former portion only which forms carburetted hydrogen; the carbonaceous matter mixed with it precipitates as black flakes, and must be separated by filtration. Iron also frequently contains traces of phosphorus and sulphur, in which case phosphuretted and sulphuretted hydrogen are formed.

1 at. Fe, and 1 at. HCl, form
1 at. Fe Cl, and 1 at. H.

350 Parts of iron require 455 parts of anhydrous hydrochloric acid, or 1750 parts of spec. grav. 1·130 (=26 per ct. acid), and consequently in the proportions we have adopted the acid is not sufficient to dissolve all the iron, which possesses this double advantage that only protochloride is formed, and any other metals which the iron filings are likely to contain, as copper, for instance, remain behind. The neutral solution, even in the presence of iron, rapidly absorbs oxygen from the air, and acquires a yellow pellicle, consisting of $Fe_2Cl_3 + 3(Fe_2O_3HO)$, at the same time a portion of the chlorine remaining in the solution; thus from

36 at. FeCl, 18 at. O, and 9 at. HO, are formed,
11 at. Fe_2Cl_3, and 1 at. $Fe_2Cl_3 + 3$ (Fe_2O_3 HO.)

In order to avoid this decomposition, it is necessary to add more hydrochloric acid, and commence the evaporation in a retort. At first the evaporation must be carried on rapidly, and only towards the end of the process, when the mass acquires a syrupy or pasty consistence, should the heat be reduced to a gentle one, otherwise from the combined action of air and heat (the former of which possesses less power at first, on account of the evolution of vapour) the salt becomes yellow.

The solution intended for crystallization must not, for the same reason, be exposed to the open air.

Properties. — Crystallized protochloride of iron forms clear green transparent rhombic pyramidal

crystals, which evaporated to dryness form a white powder, with a shade of greenish yellow; it is odourless, has at first a pungent saline, and then a sweetish astringent taste. In water and alcohol it readily dissolves; the solutions have an acid reaction. In the air it effloresces, and, absorbing oxygen, a brownish-yellow powder is formed, as previously related; in the fluid portion is now contained perchloride of iron, and sulphocyanide of potassium causes a red colour in it:

1 at. Fe_2Cl_3, and 3 at. $KCyS_2$, form
1 at. $2Fe + 3CyS_2$, and 3 at. KCl.

If the salt is kept in vessels not thoroughly air-tight, it gradually oxidizes without exactly effloresing, and acquiring a yellow colour is no longer perfectly soluble. The decomposition proceeds, however, very slowly, and even in the salt which has effloresced there remains, for some months, a considerable portion of protochloride of iron. Heated to redness, it almost entirely volatilizes, forming a white sublimate, if the air be excluded, but otherwise is partially converted into perchloride and iron, which latter remains behind as peroxide.

Any contamination with *copper* causes the solution when heated with solution of ammonia to assume a deep blue colour, which remains in the liquid, whilst the protoxide of iron precipitates.

FERRUM SESQUICHLORATUM.

Ferri Perchloridum.—Perchloride of Iron.

FORMULA: $Fe_2Cl_3 + 6HO$.

Preparation.—1 Part of metallic iron is treated as in the foregoing preparation, with 4 parts hydrochloric acid, spec. grav. 1·130; the solution filtered, 2 parts more of hydrochloric acid and 1 of nitric

spec. grav. 1·20 added, and the whole heated in a flask until the brownish-yellow vapours cease to be evolved; a part of the solution is then poured into a dish and evaporated, with constant stirring, to a syrup, or until a small portion dropped on a piece of porcelain solidifies on cooling (this it will do when the solution is reduced to four times the weight of the iron dissolved in it); the dish is now put on a glass plate, and covered with a bell glass. To prevent its attracting moisture from the air, the edge of the bell glass is greased. The fluid commences to crystallize in a day or two, and when converted into a solid mass, the dish is warmed for a moment, the mass, which is readily separated, must be broken up, put in a bottle, and kept in a dark place.

The salt is more rapidly dried by continuing to stir the fluid, after removing from the fire, until entirely cold. 1 Part of iron yields nearly 4 of crystallized chloride.

Recapitulation.— Iron dissolved in hydrochloric acid forms, as has been shown in the preceding article, protochloride of iron. In order to convert this into perchloride, half as much more chlorine is necessary, consequently the addition of 2 parts of hydrochloric acid to the 4 parts already contained. The action of some other body is required to place this in a condition to give up its chlorine; nitric acid answers this purpose, and the change of elements is as follows:—

6 at. Fe, and 6 at. ClH, form
6 at. FeCl and 6 at. H.

Further,

6 at. FeCl, 3 at. ClH, and 1 at. NO_5, form
3 at. Fe_2Cl_3, 1 at. NO_2, and 3 at. HO; the NO_2, forming in the air NO_4.

2100 Parts of iron require 2730 + 1365 = 4095 parts of anhydrous hydrochloric acid, or 10500 + 5250 =

15750 parts of spec. grav. 1.130; and 675 parts of anhydrous nitric acid, or 2500 parts of spec. grav. 1·20. As in making the protochloride of iron, only 4 parts of acid are ordered for 1 part of iron, the excess of the latter remaining in the filter. That converted by the additional hydrochloric and nitric acids into sesquichloride can only be evaporated over the fire to the point at which it crystallizes, and not, as is frequently done, to dryness, otherwise it partially decomposes, forming a reddish-brown mass, which on treating with water leaves a residue of oxide of iron. I found the chloride of iron, containing 6 at. of water,* lost by this latter treatment about half its weight; the residue consisting of 1 at. perchloride of iron, 2 at. peroxide of iron, and 1 at. of water; consequently, 6 at. of water are decomposed, 6 at. of hydrochloric acid and 11 at. of water being given off; for,

3 at. $Fe_2Cl_3 + 6HO$, form
1 at. $Fe_2Cl_3 + 2$ at. $Fe_2O_3 + 1$ at. HO, as residue, and
6 at. HCl, and 11 HO, as loss.

The loss of weight also agrees with the atomic weight, as 3 at. of crystallized perchloride of iron = 8112; 1 at. anhydrous perchloride of iron + 2 at. peroxide of iron + 1 at. water = 4142, whilst 6 at. hydrochloric acid and 11 at. water = 3966. Moreover, the residue contains a trace of protochloride of iron, arising from the decomposition of a very small quantity of perchloride into protochloride and free chlorine.

Properties.—The perchloride of iron is seldom obtained in well-defined crystals, but usually in corrugated masses, or a crystalline powder of a

* The water of crystallization of chloride of iron is stated in various proportions, viz., 4, 5, and even as high as 12 at. water. Repeated analyses of the salt obtained in the process just described always yielded me such a proportion of oxide of iron as corresponded to the formula $Fe_2Cl_3 + 6HO$; *i.e.* 49 parts of salt precipitated by ammonia gave 17·85 oxide.

brownish-yellow colour, which, under a powerful magnifier, appears as an aggregation of yellow transparent rhombic tabular crystals. It has a slight smell of chlorine, powerful acid reaction, and a pungent saline, astringent, disagreeable taste. In water, alcohol, and ether, it is readily soluble. In the air it rapidly deliquesces, forming a brownish-yellow liquid;* exposed to the light the salt becomes of a lighter colour, giving off a third of its chlorine and becoming protochloride; for these reasons the action of air and light must be avoided. At a gentle heat it fuses in its water of crystallization, but by further action of the heat it becomes decomposed as just described; on continuing to heat the dry mass to redness, the remainder of the water is given off, together with free chlorine and protochloride of iron, from decomposition of a portion of the perchloride of iron; another portion of the latter combined with oxide sublimes as a basic chloride, the residue, consisting of an iron-gray mass, when finely rubbed up forms a dark crimson powder, consisting of pure oxide. Any contamination of this preparation with protochloride is known by the blue precipitate the latter forms with ferrocyanide of potassium; (*vide* AMMON. CHLORAT. FERRATUM).

FERRUM IODATUM.

Ferri Iodidum.—Iodide of Iron.

FORMULA: $FeI + 4HO$.

Preparation.—In a flask capable of containing 16 parts of water, are placed 8 parts of water and 1 part of iron filings, to which are gradually added 4 parts of iodine, with the precaution that one portion has entirely entered into combination before another is

* On this account it is convenient to keep the preparation dissolved in its weight of water ready for use.

added. The solution is frequently agitated until the colour, at first a dark brown, is converted into a deep green; it is then filtered, the clear liquid poured into a clean iron dish, and evaporated until a portion dropped on a piece of cold porcelain, solidifies; the whole is now poured on to a clean sheet of iron, and so soon as it has hardened, the grayish-green crystalline compound is placed, still hot, in well-stopped bottles. The produce will be 6 parts.

Recapitulation.—The formation of the iodide of iron has been explained under the article AMMONIUM IODATUM. The evaporation of the solution is conducted in an iron dish to prevent as much as possible the formation of peroxide and per-iodide of iron, which under these circumstances is but slight. The oxygen of the air will of course act on the surface of the liquid, oxidizing a portion of the iron, the iodine thus separated uniting with another portion of the iodide to form per-iodide.

6 at. FeI, and 3 at. O, form
1 at. Fe_2O_3, and 2 at. Fe_2I_3.

From this cause the solution during the evaporation acquires a trace of brown colour. The evaporation must not be pushed further than the point previously indicated, otherwise free iodine will be given off. It is therefore an error to evaporate it quite to dryness, as is frequently done, the grayish-brown hydroscopic residue consisting in this case of proto-iodide, per-iodide, and peroxide of iron; with water it forms a brownish-yellow solution, and an insoluble residue consisting of peroxide and per-iodide of iron. In order more clearly to explain this decomposition, take 4 at. proto-iodide of iron, 1 at. of water, and 2 at. oxyyen:

4 at. FeI, 1 at. HO, and 2 at. O, form
1 at. Fe_2I_3, 1 at. Fe_2O_3, and 1 at. HI.

The hydriodic acid thus formed is converted during

evaporation into iodine and hydrogen. At the same time, from the action of water on a part of the per-iodide of iron, the latter is converted into peroxide of iron and free hydriodic acid (another source of free iodine).

1 at. Fe_2I_3, and 3 at. HO, form
1 at. Fe_2O_3, and 3 at. HI.

The process of forming the iodide by rubbing together 1 part of iron and 4 of iodine, either dry or sprinkled with a few drops of water, is by no means to be recommended, as the mass thus obtained dissolves in water with a brown-yellow colour, leaving a residue of metallic iron and peroxide containing per-iodide.

Properties.—Proto-iodide of iron prepared as we have directed is a dry greenish-gray crystalline mass, odourless, of a sweetish astringent taste somewhat resembling iodine. Water and alcohol dissolve it, when freshly prepared, to a greenish solution having an acid reaction. In the air it deliquesces somewhat rapidly, forming per-iodide and peroxide of iron. Even in closed vessels it becomes decomposed, owing to the water it contains ; at first it acquires a grayish-brown almost metallic lustrous appearance, and gives off the smell of iodine ; it afterwards becomes moist, the per-iodide dissolving in the water that separates from the proto-iodide, and remaining undecomposed. As soon as the preparation has begun to decompose it forms with water a solution more or less yellow or brown ; from this is deposited peroxide of iron containing per-iodide, which after the most careful washing is never freed from all traces of iodine. Gently warmed it melts, and by a further action of heat, water and air, continually evolves iodine vapours, and leaves as a residue the grayish-brown hydroscopic mass consisting of proto-iodide, per-iodide and peroxide. If the dried mass is heated to redness, all the iodine is given off, and the iron remains as oxide.

FERRUM OXIDATUM HYDRATICUM.

*Ferri Oxidi Hydras.—Ferrum Oxidatum Fuscum.—Crocus Martis Aperitivus.—Hydrated Peroxide of Iron.—Brown Oxide of Iron.**

FORMULA:

(*a*)	$Fe_2O_3 + HO$	with	10·07	per ct. water.
(*b*)	$2Fe_2O_3 + 3HO$	,,	14·42	,, ,,
(*c*)	$3Fe_2O_3 + 5HO$	,,	15·77	,, ,,
(*d*)	$2Fe_2O_3 + 5HO$	,,	21·93	,, ,,
(*e*)	$3Fe_2O_3 + 8HO$	,,	23·08	,, ,,
(*f*)	$Fe_2O_3 + 3HO$	,,	25·20	,, ,,

Preparation.—Oxide of iron forms with water several hydrates; the methods by which they are obtained are given in the same order as the formula.

(*a*) *The Monohydrate.*—13 Parts of protosulphate of iron are dissolved in 40 parts of pure water in a clean iron vessel, the solution heated to boiling, and, with constant stirring, finely powdered crystallized carbonate of soda is added as long as it causes any effervescence and a filtered portion is not rendered turbid by soda solution; 14 parts of the carbonate will be requisite. 1 Part of powdered chlorate of potash is now at once added, and the whole allowed to boil for half an hour, then poured into a capacious dish, diluted with a large quantity of water, the brown precipitate allowed to subside, the supernatant liquor decanted, the precipitate thrown on a linen strainer and dried with a gentle heat. The product is about 4 parts.

Carbonate of potash may be substituted for carbonate of soda, but this is not advisable; in the first place it is more expensive, and secondly, it generally contains silica which contaminates the precipitate.

* Also, but improperly, called carbonate of iron.

(*b*) *The Sesquihydrate.*—Sulphate of iron is precipitated as in (*a*) with carbonate of soda, the grayish-white precipitate exhausted with water and dried in the air with a gentle heat. 13 Parts of sulphate of iron yield somewhat more than 4 parts.

(*c*) *With one atom and two-thirds of water of hydration.*—The precipitate (*b*) sometimes contains rather more than an additional per ct. of water, and then forms this hydrate. This difference is probably due to the time occupied in drying, or what amounts to the same thing, in oxidizing it.

(*d*) *With two-and-a-half atoms of water.*—The grayish-white precipitate obtained under (*b*), after washing, is thrown on a linen cloth and strongly pressed; some bladders are then about half filled with it, their upper ends moistened with water, bound tightly with thread, and suspended in a tolerably warm place. As soon as the bladder feels dry externally, it is opened, the contents spread in a flat dish, and as soon as cold powdered and exposed in a moderately warm place for 14 days, or if only in the air, for from 4 to 6 weeks, until on treatment with hydrochloric acid it gives no effervescence. 13 Parts of sulphate of iron yield nearly 5 parts.

(*e*) *With two-and-two-thirds atoms of water.*—The precipitate (*d*), similarly to (*b*), contains very frequently an additional per ct. of water. The reason is probably the same.

(*f*) *With three atoms of water.*—16 Parts of protosulphate of iron are agitated in a flask, capable of holding at least four times as much as the materials used, with 16 parts water, 3 of concentrated sulphuric acid, and 4 of nitric acid, spec. grav. 1·20, as long as brownish-yellow vapours are given off; a drop is taken out at the end of a glass rod, and mixed with a drop of solution of ferridcyanide of potassium; if this causes only a brown colouration, the oxidation of the iron is perfect, but if there be

a trace of blue, more nitric acid is necessary. If not heated too strongly at first, 4 parts of nitric acid are sufficient entirely to oxidise 16 parts of protosulphate of iron. The brown solution is diluted with a considerable quantity of water, precipitated with (about 32 parts of) Liquor ammonia, spec. grav. 0·960, the precipitate washed by decantation, and lastly collected in a linen strainer, pressed and dried by a gentle heat. The yield is about 6 parts.

If the oxide of iron is intended as an antidote to arsenic, it is suspended in so much water that its weight is nine times that of the protosulphate used.

When the fixed alkalies or their carbonates are employed as precipitates, the precipitate always contains traces of them which cannot be removed by washing. For employment in the arts this is of no consequence.

Recapitulation.—(*a*) Protosulphate of iron and carbonate of soda exchange acids, carbonate of iron precipitating, combined with 1 at. of water, as a white voluminous hydrate, the sulphate of soda remaining in solution.

1 at. $FeO + SO_3 + 7$ HO, and
1 at. $NaO + CO_2 + 10$ HO, form
1 at. $FeO + CO_2 + HO$,
1 at. $NaO + SO_3$, and 16 at. HO.

1738 Parts of protosulphate of iron require 1790 parts of crystallized soda. Thrown down at the ordinary temperature, this precipitate is exceedingly bulky, and in spite of every precaution becomes partially oxidized in washing, absorbing oxygen and giving off the carbonic acid * and a portion of water, hydrated peroxide being formed. The process is expressed in the following formula.

---

* Carbonic acid forms with peroxide of iron no permanent combination.

4 at. $FeO + CO_2 + HO$, and 2 at. O, form
1 at. $2\,Fe_2O_3 + 3\,HO$, 4 at. CO_2, and 1 at. HO.

When precipitated at the boiling temperature, a rather larger portion is oxidized, but the quantity is constant (for 105 parts of precipitate, 16 parts), so that 100 parts of the boiled precipitate contain about 11 parts of hydrated oxide of iron ($2Fe_2O_3 + 3HO$), and is moreover obtained in a compact form. On account of the considerable evolution of carbonic acid which takes place, the carbonate of soda must be gradually added. One important advantage in the hot precipitation is that the compact precipitate thus obtained may be readily washed without perceptible change.

If the precipitate is suspended in water and (on account of the green or grayish oxide it contains) boiled with a somewhat large proportion of chlorate of potash, all the oxygen of the latter is absorbed by the protoxide of iron, which being converted into peroxide, is precipitated with half the quantity of water it contained as carbonate of iron; all the carbonic acid is given off, and the supernatant liquid, in addition to the sulphate of soda previously there, contains chloride of potassium.

12 at. $FeO + CO_2 + HO$, and
1 at. $KO + ClO_5$, form
6 at. $Fe_2O_3 + HO$, 12 at. CO_2, 6 at. HO,
and 1 at. KCl.

In order to convert the whole of the protoxide of iron contained in the 12 at. or 20,850 parts of protosulphate of iron into peroxide, 1532 parts of chlorate of potash are requisite. The proportion specified, 1 part to 13 of protosulphate, is more than sufficient, as it has been already shown that the carbonate contains a considerable proportion of peroxide. If the chlorate of potash is added gradually instead of at once, it is very probable that for want

of sufficient oxygen the black proto- and peroxide (magnetic oxide) will be formed, which no addition of chlorate of potash will oxidize further.

(*b*) (*c*) When the precipitate (*a*), after being washed with exposure to the air, is, without boiling with chlorate of potash, dried in the air, from the action of the oxygen of the latter, all the protocarbonate gives off its carbonic acid, and one-fourth or one-sixth of its chemically-combined water, and is converted into peroxide containing one-and-a-half or one-and-two-thirds of water of hydration :—

4 at. $FeO + CO_2 + HO$, and 2 at. O, form
1 at. $2\,Fe_2O_3 + 3\,HO$, 4 at. CO_2, and 1 at. HO.

That with one-and-two-thirds water of hydration,—

6 at. $FeO + CO_2 + HO$, and 3 at. O, form
1 at. $3\,Fe_2O_3 + 5\,HO$, 6 at. CO_2, and 1 at. HO.

(*d*) (*e*) When the carbonate of soda precipitate well washed and pressed, is, without the treatment with chlorate of potash, dried in bladders instead of in the open air, the pores of the membrane allow all the water to escape and then close; consequently, by this method a higher oxidation will scarcely occur. As soon as the bladder is opened, and the contents exposed to the air, a considerable evolution of heat takes place, and the greenish-white colour is, with the evolution of aqueous vapour and carbonic acid, exchanged for a brown; the chemical action of this is that the hydrated protocarbonate loses its carbonic acid, acquiring in exchange $\frac{1}{2}$ at. of oxygen and $\frac{1}{2}$ at. of water :—

2 at. $FeO + CO_2 + HO$, 1 at. O, and 1 at. HO, form
1 at. $Fe_2O_3 + 3HO$, and 2 at. CO_2.

The conversion does not instantly occur, but after the first powerful action has ceased a considerable quantity of protoxide remains, which becomes gradually decomposed in the same manner.

The rise of temperature consequent on the contact of the carbonate with air can scarcely be due to the fixing of the oxygen,—that is, its conversion from the gaseous into the solid state, as in exchange for every atom of oxygen which is fixed, two atoms of carbonic acid are given off as gas, and these will abstract all the heat which the oxygen may give out; but the reason, in all probability, lies in the energy with which the protoxide absorbs oxygen to become peroxide. The heat evolved is sufficient to cause a small portion of water to be given off with the carbonic acid, which together with that necessary for the constitution of this hydrate is replaced during the gradual oxidation of the remainder.

According to the preceding, this preparation should have the formula $Fe_2O_3 + 3HO$, that is, become a terhydrate. We know however from what has been said under the article (*a*), that the freshly prepared precipitate is not a pure proto-salt, but contains about 11 per ct. of sesqui-hydrated peroxide. 11 Per ct. of the sesqui-hydrated peroxide and 89 per ct. of the hydrated protoxide correspond to 1 at. of the former and 22 at. of the latter, which is equal to 11 at. of the terhydrated peroxide:—

1 at. $2\,Fe_2O_3 + 3HO$, and 11 at. $Fe_2O_3 + 3HO$, have the empirical formula
$13\,Fe_2O_3 + 36HO$, which nearly corresponds to
$3Fe_2O_3 + 8HO$.

This hydrate sometimes contains more than 1 per ct. of water less, and corresponds to $2Fe_2O_3 + 5HO$. The mother liquors obtained under (*b*) (*c*) (*d*) (*e*) can be evaporated for Glauber's salts.

(*f*) If the iron be precipitated from a solution which has been entirely converted into a persalt, the precipitate will of course contain no protoxide. For this purpose the sulphate of iron is previously treated with nitric acid. The latter gives up 3 at. of its oxygen, which uniting to 6 at. of protoxide of

iron form 3 at. of oxide. 3 At. of peroxide of iron require to form a soluble neutral sulphate, 9 at. of sulphuric acid, consequently to 6 at. of protosulphate of iron 3 at. of sulphuric acid must be added. The nitric oxide $=NO_2$ to which the nitric acid is thus reduced, when in contact with the air again combines with 2 at. of oxygen and appears as brownish-yellow vapours $=NO_4$.

6 at. $FeO + SO_3 + 7HO$, 3 at. $SO_3 + HO$, and 1 at. NO_5, form
3 at. $Fe_2O_3 + 3SO_3$, 45 at. HO, and 1 at, NO_2.

10425 Parts of sulphate of iron require 1839 parts of hydrated sulphuric acid and 675 parts of anhydrous or 2500 parts of nitric acid of 27 per ct. (spec. grav. 1·20). As at the moment when the iron becomes fully oxidized the mixture is subjected to a violent effervescence, the vessel containing it must be tolerably capacious, and in case of its coming over it is well to have an empty dish in readiness. That all the iron is converted into peroxide is proved by ferridcyanide of potassium, which having no action on persalts gives with protosalts a blue precipitate; this precipitate (Turnbull's blue) is a compound of 1 at. of ferridcyanide of potassium and 4 at. of a double cyanide of iron (Prussian blue), which, to 3 at. of protocyanide, contains only 1 at. of percyanide of iron, and is thus formed:

12 at. $FeO + SO_3$, and 5 at. $3KCy + Fe_2Cy_3$, form
12 at. $KO + SO_3$, and $(3KCy + Fe_2Cy_3) + 4(3FeCy + Fe_2Cy_3)$

The whole of the protoxide in the protosulphate of iron can be converted into peroxide without the additional sulphuric acid, but the process is more expensive, in so much as the sulphuric acid will have to be replaced by an equivalent quantity of

nitric acid, in order to dissolve all of the peroxide formed; and the mixture in this case would be persulphate and pernitrate of iron; or,

3 at. Fe_2O_3, 6 at. SO_3, and 3 at. NO_5, form
2 at. $Fe_2O_3 + 3SO_3$, and 1 at. $Fe_2O_3 + 3NO_5$.

When caustic solution of ammonia (oxide of ammonium) is added to the persulphate of iron, it combines with the sulphuric acid of the latter to a readily soluble salt, whilst the oxide of iron precipitates in combination with 3 at. of water.

3 at. $Fe_2O_3 + 3SO_3$, 9 at. $NH_3 + HO$, and
9 at. HO, form
9 at. $NH_4O + SO_3$, and 3 at. $Fe_2O_3 + 3HO$.

7500 Parts of persulphate of iron (obtained from 10425 parts of protosulphate, &c.,) require 1917 parts of anhydrous ammonia, or 19170 parts of Liq. ammonia, spec. grav. 0·960 (=10 per ct. anhydrous ammonia).

The sulphate of ammonia is obtained from the supernatant liquor by evaporation.

In using a caustic fixed alkali, the process is the same as with a carbonate; in the latter case the carbonic acid will be given off.

This oxide of iron is also employed as an antidote for arsenic, and for this purpose it should be used in the moist state, to insure a speedy and certain action. When the hydrate weighs nine times as much as the protosulphate used, 24 parts contain 1 part of terhydrated peroxide of iron, or $\frac{3}{4}$ of a part of anhydrous peroxide; for,

2 at., or 3475 parts, of protosulphate of iron give 1 at., or 1338 parts, of terhydrated peroxide of iron, or 1000 parts of anhydrous peroxide of iron; for 1 part of protosulphate =9 parts of the above mixture of hydrate and water; or, 0·38 parts $Fe_2O_3 + 3HO$; or, 0·28 Fe_2O_3; or, what is the same thing, $2\frac{3}{8}$ parts of protosulphate of iron =24 parts

of moist hydrate; 1·01 $Fe_2O_3 + 3HO$; or, 0·75 Fe_2O_3.

Properties.—The hydrated oxides of iron obtained by the processes (*a*) (*b*) and (*c*), form a dirty yellow-brown amorphous powder; those from (*d*) (*e*) and (*f*) have a reddish-brown tint. They are odourless and tasteless, insoluble in water, but dissolve readily in hydrochloric acid, forming a golden-yellow solution. Heated to redness, they lose their water. If they have not been carefully washed, water, when boiled on them, gives, with solution of chloride of barium, a precipitate of sulphate of baryta. If on treatment with hydrochloric acid effervescence is caused, *carbonic acid* is present; this may arise from the excess of carbonate of soda not being washed out,* or if common water has been used instead of distilled, it will be due to carbonate of lime; it being taken for granted that all the iron is entirely converted into oxide (and that the precipitates (*b*) (*c*) (*d*) (*e*) have been exposed a considerable time to the air). If carbonate of lime is present, it may be detected, in the feebly-acidified solution, by oxalate of ammonia. If the hydrochloric acid solution gives, with ferridcyanide of potassium, a blue precipitate, it contains *protoxide; (vide (f))*. If after dissolving in hydrochloric acid there is a white gelatinous residue, soluble in potash, it is *silica*, arising from the use of a potash containing silica. Any *oxide of copper* present is known by the blue colour it acquires when shaken with a solution of carbonate of ammonia. Should the colour not be perfectly evident, supersaturate with acetic acid, and add solution of ferrocyanide of potassium, which with the smallest trace of copper causes a brownish-red precipitate.

The terhydrated oxide of iron which exists in the

* Which, as I have already remarked under (*f*), never entirely happens.

moist mass (*vide* (*f*)) loses, by long standing, the half of its chemically-combined water, becoming crystallized instead of amorphous, is no longer soluble in acetic acid, and dissolves with difficulty in tartaric. It is therefore recommended, about every six months, that the hydrate, kept as an antidote to arsenic, be redissolved in hydrochloric acid and precipitated with ammonia.

FERRUM OXIDATUM RUBRUM.

Ferri Oxidum.—Crocus Martis Astringens.—Red Oxide of Iron.

FORMULA: Fe_2O_3.

Preparation.—A portion of the hydrated oxide of the previous article (that under (*b*) is preferable, as being least costly) is tightly pressed into an earthen crucible, the latter covered and gently heated as long as its contents diminish, then to very faint redness for half an hour. 7 Parts of the sesquihydrated oxide of iron give from 5 to 6 parts of oxide.

As native oxide of iron generally contains silica, it must not be substituted for this preparation.

Recapitulation.—The hydrated oxide of iron loses its water by heating, pure oxide remaining. The heating must scarcely be carried to redness, as, on account of the powerful evolution of watery vapour, a portion of the contents is thrown out of the crucible.

Properties.—The anhydrous oxide of iron is an odourless and tasteless dark crimson-red powder, perfectly insoluble in water. Hydrochloric acid dissolves it entirely, although with difficulty, form-

ng, without any gas being evolved, a golden-yellow solution, which must not give, with ferridcyanide of potassium, a blue precipitate, otherwise *protoxide* is present; (*vide* the previous article).

FERRUM OXIDATUM ACETICUM LIQUIDUM.

Liquor Ferri Acetatis.—Solution of Peracetate of Iron.

FORMULA: $Fe_2O_3 + \bar{A} + xAq$.

Preparation.—The terhydrated oxide of iron, prepared from 16 parts of protosulphate, as in the article FERRUM OXID. HYDRAT., after washing and pressing, is dried, so that, although still moist, it is friable (in which state it will weigh from 16 to 20 parts), rubbed up in a porcelain mortar with 8 parts of acetic acid, spec. grav. 1·045, the whole poured into a bottle, and, with frequent shaking, allowed to digest two days, at the ordinary temperature; then, if all the oxide is not dissolved, acetic acid added in small portions, 2 parts more will be ample, and the solution diluted with water until its weight is 36 parts.

Allow it to stand some days for all impurities to subside, then strain and keep in a closed vessel, in a cool dark place.

Recapitulation.—Hydrated oxide of iron, in a dry state, dissolves in acetic acid with difficulty and but partially; consequently they must be brought in contact whilst the oxide is recently precipitated. In order that the solution be not too dilute, the greater portion of the water is removed by pressure. From the quantity of acetic acid necessary for the solution of the precipitate (8 – 10 parts, of a spec. grav. 1·045, to the oxide from 16 parts of sulphate

of iron), it appears that the salt corresponds to the formula $Fe_2O_3 + \bar{A}$. 16 Parts of sulphate of iron yield $4\frac{3}{5}$ parts of anhydrous oxide, 8 – 10 parts of acetic acid, spec. grav. 1·045, contain $2\frac{8}{9}$ to $3\frac{2}{5}$ of anhydrous acid; the atomic weight of oxide of iron is 1000, that of acetic acid 638. If rather more than 8 parts of acetic acid of the proper weight are required, it is because the strength of the acid cannot be exactly determined from its specific gravity; a slight per centage more or less scarcely causing the areometer to fall or rise. Heat is unnecessary for the solution of the hydrate, but rather injurious, as it may cause a separation of a portion of oxide, which will require a large excess of acid again to take it up.

In order to obtain the solution of a uniform strength, it should always be brought to one certain weight. As 16 parts of protosulphate of iron form $4\frac{3}{5}$ parts of oxide, 36 parts of solution contain the same quantity, or 8 parts contain 1 of oxide.

Properties.—Thus prepared, the liquid per-acetate of iron is a dark, reddish-brown, clear fluid, transparent only in moderate layers, of spec. grav. 1·130 to 1·135. It has the odour of acetic acid, with an acid, astringent, ferruginous taste. Caustic ammonia causes in it a bulky, reddish-brown precipitate of peroxide of iron; the supernatant liquid must be colourless; if it has a blue tint, this denotes *copper*, and hydrosulphuret of ammonia causes a brownish or black precipitate of sulphuret of copper.

9 Parts of this liquid form, with 2 parts alcohol 80 per ct. and 1 part of acetic ether, Tinctura ferri acetici ætherea Klaprothii. 21 Parts of this tincture contain 2 parts of peroxide of iron.

A very disagreeable property of the liquid acetate of iron and its tincture is, that after keeping a longer or shorter time it becomes gelatinous, and a portion of the iron separates as a basic acetate of

iron. This decomposition does not arise from an error in making it, or the employing impure materials, but from the weak affinity existing between the peroxide of iron and the acetic acid, and the tendency which the iron has to form, with the acid, a basic salt, which is insoluble in acetic acid; and it is on account of this insolubility that excess of acetic acid will not again dissolve it. The decomposition of the tincture is avoided by making only small portions at a time. A decomposed aqueous solution should be filtered, and, when well drained, the contents of the filter dissolved in dilute hydrochloric acid, precipitated with ammonia, washed, pressed, added to the filtered liquors, and allowed to digest some days at the ordinary temperature, when most of it will dissolve. The liquid is then to stand, and is strained from the precipitate.

FERRUM OXIDATUM CITRICUM AMMONIATUM.

Ferri Ammonio Citras.—Ammonio Citrate of Peroxide of Iron.

FORMULA:

$$(5NH_4O + 2\overline{Ci} + 6HO) + 4(Fe_2O_3 + \overline{Ci} + 3HO).$$

Preparation.—Hydrated oxide of iron, prepared (according to (*f*) under that article) from 16 parts of protosulphate of iron, after being washed, and whilst still suspended in water, is treated with 33 parts of citric acid that has previously been dried at a gentle heat; when the hydrate is dissolved carbonate of ammonia is added to the brownish-yellow solution (nearly 14 parts will be sufficient), and this evaporated with a gentle heat to dryness. The dried mass, after powdering, is kept in a closed

vessel, and should weigh about one-third more than the citric acid used.

Recapitulation.—Freshly precipitated hydrated oxide of iron is entirely soluble at the ordinary temperature in an equivalent weight of citric acid; that which has been kept under water is less so, whilst the dried is still less soluble. One-half more citric acid than the equivalent quantity is here ordered, as citrate of ammonia is also to be formed. Citric acid dried with a gentle heat consists of $C_{12}H_5O_{11} + 3HO$ or $\overline{Ci} + 3HO$, and if we consider carbonate of ammonia as $NH_4O + 2CO_2 + HO$ (the composition of that generally met with in shops), the following formula explains the process:

2 at. Fe_2O_3, 3 at. $\overline{Ci} + 3HO$, and 3 at. $NH_4O + 2CO_2 + HO$, form

1 at. $3NH_4O + \overline{Ci} + 3HO$, 2 at. $(Fe_2O_3 + \overline{Ci} + 3HO)$, 6 at. CO_2, and 3 at. HO.

2000 Parts of peroxide of iron require 7200 parts of hydrated citric acid, and 2964 parts of carbonate of ammonia. As 16 parts of protosulphate of iron form $4\frac{3}{5}$ parts of peroxide, the latter require 33 parts of hydrated citric acid, and almost 14 parts of carbonate of ammonia. During evaporation $\frac{1}{6}$ of the ammonia is given off, consequently the preparation has the formula assigned to it at the commencement of this article.

Properties.—Dry ammonio citrate of iron has the appearance of a brownish-yellow resinous mass, forming a greenish-yellow powder, having a somewhat pungent saline taste, becoming ferruginous; it attracts moisture from the air and acquires after some days the consistence of an extract. In water it entirely dissolves, with a greenish-yellow, inclining to a sulphur-yellow colour; the solution should give with ferridcyanide of potassium no green or

blue colour, far less a blue precipitate, in either of which cases protoxide is present.

FERRUM OXIDATUM PHOSPHORICUM.

Ferri Perphosphas.—Perphosphate of Iron.

FORMULA : $Fe_2O_3 + P_2O_5 + 8HO$.

Preparation.—16 Parts of protosulphate of iron are converted into persulphate with nitric acid as in the article FERR. OXIDAT. HYDRAT. (*f*), the solution diluted, and a solution of ordinary crystallized phosphate of soda added as long as it causes a precipitate. From 33 to 34 parts of the soda salt will suffice. After subsiding, the supernatant liquor is decanted and the residue dried with a gentle heat. The weight of the product will be about 13 parts.

Recapitulation.—When aqueous solutions of persulphate of iron and phosphate of soda are brought in contact, 1 at. of peroxide of iron, 1 at. of phosphoric acid, and 8 at. of water, combine to form an insoluble compound. One might suppose that 1 at. of phosphate of soda would suffice to 1 at. of persulphate of iron, but experience shows that at least $1\frac{1}{2}$ at. of the former are necessary to cause the precipitation as phosphate of the whole of the iron in the solution, and the process is thus expressed :

2 at. $Fe_2O_3 + 3SO_3$, and 3 at. $2NaO + HO + P_2O_5 + 24Aq.$, form
2 at. $Fe_2O_3 + P_2O_5 + 8HO$, 6 at. $NaO + SO_3$, 1 at. P_2O_5, and 59 at. HO.

4 At. or 6950 parts of protosulphate of iron require, after being converted (by nitric acid and 2 at. sulphuric acid) into persulphate, 13476 parts of crystallized phosphate of soda. The liberated sulphuric acid is exactly sufficient to neutralize all the soda,

although from the free phosphoric acid present it is certainly more correct to consider that this saturation is divided between the two acids, so that with the addition of 2 at. of water the solution may be supposed to consist of

4 at. $NaO + SO_3$, 1 at. $NaO + 2SO_3$, and
1 at. $NaO + 2HO + P_2O_5$.

The acid solution (which as has been previously shown contains no trace of iron), when a considerable excess of phosphate has been used, may be neutralized with lime and used for Glauber's salts.

Properties.—Phosphate of iron thus prepared is a white powder with a slightly yellow tinge, odourless and tasteless, the particles of which when highly magnified appear transparent and crystalline. At 212° Fah. it loses half its water, and at a red heat becomes anhydrous without changing its colour. In water it is insoluble; hydrochloric acid readily dissolves it to a golden-yellow solution, which when diluted with water must give with ferridcyanide of potassium no blue precipitate, otherwise it is not free from protoxide of iron; (*vide* AMMON. CHLORAT. FERRATUM).

FERRUM OXIDATUM SULPHURICUM.

Ferri Persulphas.—Persulphate of Iron.

FORMULA OF THE DRIED SALT: $Fe_2O_3 + 3SO_3 + 9HO$.

Preparation.—16 Parts of protosulphate of iron are oxidized as directed under the article FERRUM. OXIDAT. HYDRAT. (*f*), the solution heated in a porcelain dish until all adhering nitric acid is given off (this point is known by indigo solution being no longer decolourized), then diluted with water until the whole weighs 32 parts, and kept in a dark place. If required in a dry form the solution is

evaporated, the latter part of the time in a sand bath, continually stirring with a porcelain spatula, until the mass acquires a tough resinous and on cooling brittle consistence, it is then powdered in a dry cool mortar and kept in the dark in a well-closed bottle.

Recapitulation.—As under the article FERR. OXIDAT. HYDRAT. (*f*). The persulphate of iron not being crystallizable, and as its evaporation to dryness is attended with some difficulty, it may with advantage be kept in the form of solution, being almost always used in this state. In the degree of concentration just given its absolute weight is double that of the protosulphate used, its spec. grav. 1·400; 28 parts contain 18 of salt, 64·25 per ct. The dry salt must be preserved from contact with the air, as it readily attracts moisture and deliquesces; both the salt and its solution must, like perchloride of iron, be guarded from the light; otherwise, though far more slowly than the chloride, they become partially reduced to protosalts, $\frac{1}{3}$ of the oxygen of the peroxide of iron and $\frac{1}{3}$ of the sulphuric acid being liberated:

1 at. $Fe_2O_3 + 3SO_3$, form
2 at. $FeO + SO_3$, 1 at. O, and 1 at. SO_3.

Properties.—Dry persulphate of iron forms either an amorphous resinous mass, somewhat resembling in appearance tannin from gall nuts, or a pale greenish-yellow powder. It is odourless, but has a pungent saline excessively bitter taste. In the air it deliquesces to a brownish-yellow solution, which reacts strongly acid, and mixes with water and alcohol in all proportions. The solution, having the spec. grav. 1·400, is brownish-yellow and almost of a syrupy consistence. Heated to redness the salt, without fusing, gradually loses its water and acid, leaving a crimson-red powder of pure peroxide. Any contamination with *protosalts* is detected by ferridcyanide of potassium, which then causes a blue

precipitate; (*vide* AMMON. CHLORAT. FERRAT.). *Copper* is present if after the oxide of iron is precipitated with excess of ammonia the supernatant liquid has a blue appearance.

FERRUM OXIDATUM VALERIANICUM.

Ferri Valerianas.—Valerianate of Peroxide of Iron.

FORMULA: $3Fe_2O_3 + 7C_{10}H_9O_3 + 2HO$; or,
$7(Fe_2O_3 + 3\overline{V}a) + 2(Fe_2O_3 + 3HO)$.

Preparation.—5 Parts of pure valerianic acid (the terhydrate) are mixed in a porcelain dish with 60 parts of water, and constantly stirring, crystallized carbonate of soda is added to the mixture until the acid is saturated (six parts of carbonate will effect this), then boiled for a few moments and allowed to cool. 3 Parts of crystallized perchloride of iron are now dissolved in a cylindrical glass vessel (or $3\frac{1}{2}$ parts of dry persulphate, *vide* this article) with 100 parts of water, and the *thoroughly cooled* solution of valerianate of soda added to the latter so long as it causes a precipitate. All the solution of valerianate of soda will be required for this purpose. The precipitate after depositing is collected on a filter and washed with only as much water as is necessary to rinse the glass cylinder; the precipitate is dried at a temperature not exceeding 70° Fah. and kept in a closed vessel. The product will nearly equal the weight of acid employed.

The liquid which filters from the precipitate is not thrown away, but distilled in a retort until nearly $\frac{2}{3}$ have passed over; this distillate is a dilute aqueous solution of valerianic acid.

Recapitulation.—The valerianic acid drives off the carbonic acid from the carbonate of soda, and uniting with the base forms a neutral salt.

1 at. $\overline{V}a + 3HO$, and 1 at. $NaO + CO_2 + 10HO$ form
1 at. $NaO + \overline{V}a$, 1 at. CO_2, and 13 at. HO.

1500 Parts of the terhydrated valerianic acid require therefore 1790 parts of crystallized carbonate of soda, or 5 parts of the former nearly 6 parts of soda. It is necessary to boil the solution to drive off all the carbonic acid. If this neutral solution is added in sufficient quantity, (as long as it causes a precipitate,) to a solution of perchloride or any persalt of iron, a dark brick-red precipitate of valerianate of iron and readily soluble sulphate of soda are formed.

3 at. $NaO + \overline{V}a$, and 1 at. Fe_2Cl_3 (or $Fe_2O_3 + 3SO_3$), form
1 at. $Fe_2O_3 + 3\overline{V}a$ and 3 at. NaCl (or $NaO + SO_3$).

4500 Parts of valerianic acid saturated with soda require 2704 parts of crystallized perchloride of iron ($Fe_2Cl_3 + 6HO$) or 3513 parts of dry persulphate of iron ($Fe_2O_3 + 3SO + 9HO$). The neutral compound of peroxide of iron with valerianic acid ($Fe_2O_3 + 3\overline{V}a$) is not precipitated, but decomposes as soon as formed into a basic salt in which—if the formula of the neutral salt is tripled—2 at. of acid are replaced by 2 at. of water, forming a salt $3Fe_2O_3 + 7\overline{V}a + 2HO$, and free valerianic acid, which holding a portion of the basic salt in solution gives to the supernatant liquor a slightly yellowish-red colour. This small portion of the basic salt may be re-obtained by very carefully saturating the acid with soda, but then a portion of the acid, as valerianate of soda, will remain in the solution. The affinity between the oxide of iron and valerianic acid is so feeble that a gentle heat will suffice to abstract the greater portion of the acid; consequently the precipitation should take place only in the cold. All the iron is thrown down by boiling, but then the precipitate will either contain only a trace of acid, or if the boiling was

continued for some time, none at all, consisting of nothing but hydrated oxide of iron, which on cooling will not again combine with the liberated acid. These facts are of great importance, and should be borne in mind in making these preparations. Even continued treatment with cold water gradually abstracts the acid, and at the same time removes a little of the oxide of iron, so that the precipitate must not be washed as long as the water passing off has an acid reaction.

From this it is evident that by simple distillation, and without the addition of any other acid the whole of the valerianic acid in the supernatant liquid may be re-obtained.

Properties.—The valerianate of peroxide of iron obtained by precipitation, is a dark brick-red, loose amorphous powder, smelling and tasting faintly of valerianic acid. Slowly heated, it gradually gives off all its acid without fusing; heated rapidly it melts (evidently with the separation of the acid from the base), and the acid volatilizes in thick combustible vapours, but at the same time undergoes decomposition, for the fumes scarcely smell of valerianic acid, but possess the characteristic odour of butyric acid $=C_8H_7O_3$. From the elements of the valerianic acid there have separated 2 at. of carbon and 2 at. of hydrogen, which combine to form 2 at. of carburetted hydrogen.

1 at. $C_{10}H_9O_3 = 1$ at. $C_8H_7O_3$, and 2 at. CH.

The residue is pure peroxide of iron. The salt behaves towards cold water like lycopodium, that is, it will not mix even when continuously rubbed with it. By warm water it is instantly wetted, but at the same time gives up a portion of its acid. Boiled with water it is entirely decomposed, into free acid and hydrated peroxide of iron, which on cooling will not again combine. The preparation is readily soluble in hydrochloric acid, and the solution when diluted will, if too much

hydrochloric acid has not been added, cause no blue colour with ferridcyanide of potassium; the peroxide of iron is subject to partial reduction to protoxide from the valerianic acid, as from acetic acid.

If the salt can be heated rapidly in a platinum spoon, without fusing, it does not contain sufficient acid.

FERRUM OXIDATUM NIGRUM.

Ferri Per et Protoxidum.—Æthiops Martialis.—Black Oxide of Iron.—Magnetic Oxide.

Formula of that prepared by the Moist way:

$$(FeO + Fe_2O_3) + HO.$$

Formula of that prepared by the Dry way:

$$(FeO + Fe_2O_3) + xFe + xC.$$

Preparation. — Since Wöhler has made known the preparation by the moist way of a black oxide of iron, always agreeing in composition, that by the dry method is scarcely to be recommended; but as it is the officinal preparation of most of the pharmacopœias, we must not overlook it.

(*a*) *By the moist way.*—16 Parts of protosulphate of iron are converted into persulphate as directed under (Ferr. Oxyd. Hydr. (*f*)); the liquid is diluted with a good portion of water, mixed with a solution of 8 parts of protosulphate in 32 parts of water, and treated with solution of caustic ammonia so long as this causes a precipitate. 24 Parts of protosulphate require about 42 parts of ammonia spec. grav. 0·960. The black precipitate is allowed to subside, the saline solution decanted, the residue thrown on a filter, dried in a gentle heat, and kept in a closed bottle. It will weigh about 7 parts.

(*b*) *By the dry way.* — A certain quantity of hydrated peroxide of iron (as the kind of hydrate employed is immaterial, the sesquihydrate may be preferred as the cheapest) is reduced in an iron mortar to a fine powder, and so much linseed oil

gradually added that the powder is thoroughly saturated, and forms a crumbling paste; oil of about half the weight of the hydrate will suffice; the mass is pressed into a black-lead crucible sufficiently capacious to hold $\frac{1}{3}$ more, the crucible is covered, and, excepting a very small opening, closely luted with clay. When the lute is dry, the crucible is placed on a brick in a good wind furnace, heated at first gently, and then more strongly, until neither flame nor smoke escape from the little aperture; it is now raised to a red heat, and this continued for half-an-hour. When thoroughly cool the crucible is opened, the black mass finely powdered, and kept in a closed bottle. The produce from 6 parts will be from $4\frac{1}{2}$ to 5 parts.

Recapitulation (*a*).—The theory of the formation of persulphate of iron has been already explained. When to the persulphate protosulphate is added, equalling half the weight of protosulphate first employed, we obtain a mixture of per- and protosulphate of iron = $(FeO + SO_3) + (Fe_2O_3 + 3SO_3)$. Ammonia precipitates the proto- and peroxide chemically combined with each other and 1 at. of water, and uniting with the sulphuric acid forms soluble sulphate of ammonia (Oxide of Ammonium).

1 at. $(FeO + SO_3) + (Fe_2O_3 + 3SO_3)$, 4 at. NH_3, and 5 at. HO, form
1 at. $(FeO + Fe_2O_3) + HO$, and 4 at. $NH_4O + SO_3$.

3450 Parts of anhydrous sulphate of magnetic oxide of iron (corresponding to 3 at. or 5214 parts of protosulphate) require 852 parts of anhydrous or 8520 parts of hydrated ammonia of spec. grav. 0·960 (=about 10 per ct. of ammonia). The precipitate is easily washed without acquiring a higher form of oxidation.

The first portion of the wash water may be evaporated for sulphate of ammonia.

(*b*) When hydrated oxide of iron is heated with

a fatty oil, the water is first given off, and then the decomposition of the oil commences ; one portion of the carbon of the oil having abstracted the oxygen of the oxide of iron, and another portion in combination with the oxygen of the oil pass off as carbonic oxide gas, whilst a third portion united to the hydrogen of the oil forms carburetted hydrogen (=CH) ; the remainder of the carbon (for the oil contains more than sufficient to convert the whole of the oxygen and hydrogen of the two substances into carbonic oxide and carburetted hydrogen) remains with the oxide of iron. At the commencement of the process other combustible products are given off from the oil, and give rise to the thick smoke. From the excess of carbon, we might expect that all the iron would be reduced to the metallic state, but although this occurs with a considerable quantity, the greater portion of the oxide only gives off as much oxygen as is necessary to convert it into the magnetic oxide. Thus it is evident that the Æthiops Martial, prepared by the dry way, is neither pure protoxide nor magnetic oxide of iron, but a mixture of carbon, metallic iron, protoxide and peroxide of iron ; which two oxides may be considered to exist as a compound, agreeing in chemical composition with the native magnetic iron ore. I found that 100 parts of a beautiful velvety black Æthiops contained—

68·82 magnetic oxide,
22·84 metal,
8·34 carbon,

100·00

This proportion corresponds nearly to 3 at. of iron and 2 at. of magnetic oxide.*

* Iron scales from the blacksmith's forge are constant in composition, and free from metallic iron; 100 parts, when freshly made, contain 54·26 of protoxide of iron, 40·14 of oxide of iron, and 5·60 of silica and carbon. The relative mixture of protoxide and peroxide corresponds to the formula $3FeO + Fe_2O_3$.

Properties (*a*).—The black oxide of iron prepared by precipitation forms a jet black mass, which finely powdered has a brownish-black tinge, and is without smell or taste. It dissolves in hydrochloric acid readily, quietly, and without a residue; the solution has a yellowish colour. (*b*) The oxide prepared by heating forms a similarly black, odourless, and tasteless mass, yielding a powder which appears entirely black. In hydrochloric acid it dissolves, yet not so readily as the former, and leaves a carbonaceous residue; the solution also, instead of going on quietly, is accompanied by evolution of hydrogen gas, from the metallic iron present. Should the gas have the smell of rotten eggs, and when passed through acetate of lead solution, cause a black precipitate (sulphuret of lead), it contains *sulphuretted hydrogen*, owing to the presence of some sulphuret of iron in the Æthiops; if in the preparation of the latter, oxide of iron has been employed which was precipitated with a fixed alkali, and not very carefully washed, the alkaline sulphate adhering to it becomes reduced by the carbon of the oil to a sulphuret of sodium or potassium, and when treated with hydrochloric acid is converted into a chloride with the evolution of sulphuretted hydrogen gas. If the colour of the preparation inclines more to brown or red, it contains, besides the magnetic oxide, unaltered *peroxide*. Excess of ammonia added to solution of chloride, and causing a blue colour in the supernatant liquor, denotes the presence of *copper*.

FERRUM PROTOXIDATUM CARBONICUM.

Ferri Carbonas.—Proto-Carbonate of Iron.

FORMULA : $(FeO + CO_2 + HO) + x(Fe_2O_3 + HO)$.

Preparation. — Under the article FERR. OXID. HYDRAT. (*a*) and (*d*), the formation of a protocarbonate of iron has been fully described. A solution of protosulphate of iron is heated to boiling in an iron or leaden vessel, and carbonate of soda gradually added so long as an effervescence is caused, the precipitate, washed by decantation, is pressed and dried in a bladder in the air. The mass when thoroughly dried is immediately transferred to bottles, which must be carefully closed and kept in a cool place. 13 Parts of protosulphate of iron form about 5½ parts.

Recapitulation.—Here again we refer to the articles (*a*) and (*d*). On account of the avidity with which the preparation absorbs oxygen, the bladder must be as free as possible from air.

Properties.—Well prepared carbonate of iron is a greenish-white odourless and tasteless powder. In perfectly closed vessels it remains unchanged and only the surface becomes a little brown from the air in the bottle above it. In the open air it soon loses its carbonic acid, and forms hydrated oxide of iron; (*Vide* FERR. OXID. HYDRAT. (*d*)). In hydrochloric acid it dissolves readily and thoroughly, with a strong evolution of carbonic acid. *Lime* and *Copper* are detected as in hydrated oxide of iron.

FERRUM PROTOXID. CARBONICUM SACCHARATUM.

Ferri Carbonas, c Saccharo.—Saccharine Carbonate of Iron.

FORMULA:

$$(FeO + CO_2 + HO) + x(Fe_2O_3 + HO) + x(C_{12}H_{11}O_{11}).$$

Preparation.—Carbonate of iron prepared as in the preceding article is mixed, after washing and pressing and whilst still moist, in a porcelain dish with finely powdered sugar half the weight of protosulphate of iron precipitated; the mass is constantly stirred, evaporated at a gentle heat to dryness, rubbed to powder and kept in a closed bottle. 13 Parts of sulphate of iron yield 12 parts of saccharine carbonate of iron.

Recapitulation.—When sugar is added to moist carbonate of iron it immediately abstracts its water and at the same time the mass acquires a deep-green colour, becomes deliquescent, and the carbonate of iron having a protecting covering of sugar undergoes no further change during the evaporation to dryness. The real use of the sugar is to prevent the oxidising action of the air on the protoxide of iron, and by this means the carbonic acid is retained in combination with the latter. The sugar may possibly in this case exert an opposing action to the formation of peroxide, as it possesses the property of reducing peroxide of copper to protoxide, (*vide* CUPR. PROTOX.), although it has not the power of converting any of the peroxide, already present, to protoxide.

Properties.—Saccharine carbonate of iron is a permanent greenish or brownish-grey powder, odourless, with a sweet and somewhat ferruginous taste. Cold water dissolves besides the sugar a small quantity of carbonate of iron; if however this solution is heated to boiling it evolves carbonic acid, and at

the same time becomes yellow and turbid from the separation of hydrated peroxide of iron. With hydrochloric acid it strongly effervesces. 100 Parts of this preparation correspond to about 45 parts of dry carbonate of iron.

FERRUM PROTOXIDATUM LACTICUM.

Ferri Lactas.—Proto-Lactate of Iron.

FORMULA: $FeO + C_6H_5O_5 + 3HO$.

Preparation.—In making this salt there are two methods which appear to me preferable to all others, but both of them have their advantages and drawbacks. The first of these is the most simple, and yields a very pure salt, but the product is small; the second method yields more, but the process is longer.

(*a*) *By means of protosulphate of iron or protochloride of iron.*—Proceed at first, as directed under the article ACID LACTICUM. In 100 parts of sour whey, 5 parts of sugar of milk are dissolved, the free acid saturated with a weighed portion of crystallized carbonate of soda, the liquid placed in a vessel exposed to the air (in summer at the ordinary temperature, in winter near a fire), and every 1 or 2 days the acid formed is neutralized with the carbonate of soda. When several days elapse without any acid reaction being perceptible, a few drops of sulphuric acid are added, so that litmus paper is slightly reddened, the solution clarified with white of egg, strained and evaporated in a porcelain dish until its weight equals about a fourth part of the whey used, and, with constant stirring, a fresh and ready prepared warm solution of so much protosulphate of iron, in twice its weight of water added to it, as is equivalent to the soda required for neutralization. The dirty gray flocculent matter which immediately forms, toge-

ther with the particles of caseine which separate during evaporation, are, after some few minutes (during which it must be kept hot), removed by straining through flannel and the clear liquid allowed to cool. The crystallization immediately commences and proceeds with rapidity, so that on the following day it forms almost a solid mass. The salt is drained on a linen cloth, washed with a little cold water, and then with a little alcohol (to remove the water); it is now spread on and covered with several thicknesses of filtering paper, and dried at a gentle heat. The product will be 4 to 5 parts.

The mother liquor on evaporation yields from $\frac{1}{2}$ to $\frac{3}{4}$ part of lactate of iron, which is however contaminated with sulphate of soda, and is better reserved for solution the next time, with the sulphate of iron. The mother liquor is now of little use, the most that can be done is to precipitate the iron from it with soda.

Instead of sulphate, chloride of iron may be used; for 18 parts of soda employed 11 parts of dried protochloride of iron will be necessary; the process resembles the preceding. In this case the mother liquor contains chloride of sodium.

(*b*) *With Metallic Iron*—The clear solution of lactate of soda prepared according to (*a*), and reduced to one-fourth the quantity of the whey used, is evaporated in a water bath to the consistence of an extract, (to about $12\frac{1}{2}$ parts or $\frac{1}{8}$ the weight of the whey used); the extract is twice exhausted with alcohol of 90 per ct. in a flask, strained, pressed, and the alcoholic solution mixed with concentrated sulphuric acid equalling in weight one-third of the soda employed; it is allowed to stand some hours, frequently shaking, the salt which separates, is strained and the solution filtered. With the latter is mixed (when 100 parts of whey are used) 40 parts of water, the alcohol distilled off to 50 parts

residue, the latter poured into a bottle, 2 parts of powdered iron added to it, the whole digested in a sand bath, frequently shaking, for about 3 hours or so long as there is any action on the iron, and filtered whilst hot. If during the digestion there has been much evaporation and any separation of the salt, it must, previously to filtration, be brought up to the original bulk with hot water. The saline crust which separates after several days is removed, the mother liquor evaporated further, this again repeated, and the last, generally black, mother liquor thrown away. The crystalline masses are washed with alcohol and dried. Should the last crystallization be much discoloured it is, when dry, again dissolved in twelve times its weight of boiling water, filtered, and crystallized. From 100 parts of whey 5 to 6 parts of salt are obtained.

Recapitulation.—(*a*) For the formation of lactic acid from sugar of milk refer to the article ACID. LACTICUM. When a concentrated solution of lactate of soda, formed by neutralizing with carbonate of soda, is mixed with protosulphate of iron, the soda combines with the sulphuric acid, and the protoxide of iron with the lactic acid; on cooling, this compound owing to its slight solubility, separates, the sulphate of soda remains dissolved. On mixing the two saline solutions, a dirty-gray precipitate of caseous and extractive matter is formed, which is separated from the liquid most quickly by flannel; if filtered through paper most of the salt would solidify on the filter. For 1 at. of lactate of soda, 1 at. of sulphate of iron will be requisite; to determine the quantity of sulphate of iron required, it is only necessary to take the quantity of carbonate of soda used for neutrallization as a guide; for as 1 at. of carbonate of soda is equivalent to 1 at. of lactate of soda; so 1 at. of soda corresponds to 1 at. of sulphate of iron. The atom of crystallized soda = $NaO + CO_2 + 10HO$; or its atomic weight is 1790; the

atom of protosulphate of iron = $FeO + SO_3 + 7HO$ is 1738; consequently, without any very great error 11 parts of crystallized soda (generally required to neutralize 100 parts of whey) may be decomposed with 11 parts of protosulphate of iron.

In using protochloride of iron, (of which the formula being $FeCl + 2HO$, 1018 parts are requisite), the theory is exactly the same, chloride of sodium being formed instead of sulphate of soda.

The lactate of iron which crystallizes out, is washed with a little cold water to remove any adhering sulphate of soda or chloride of sodium, and finally, to cause it to dry more quickly, it is saturated with alcohol. During the drying the salt quickly acquires a brown tint where the air has a free action, consequently the particles should be brought as closely together as possible, and the whole of it covered with paper. The first of the mother liquor contains a considerable quantity of salt, but of this only a small portion is recoverable, as on further evaporation the sulphate of soda begins to crystallize, and from the action of the heat the lactate of protoxide is quickly converted into uncrystallizable magnetic salt. In this change, when the further influence of the air is prevented, peroxide of iron separates as a hydrate.

20 at. $FeO + \bar{L}$, and 9 at. O, form

2 at. $(FeO + \bar{L} + 3Fe_2O_3 + \bar{L}_3)$. and 3 at. Fe_2O_3.

The oxygen required by the latter 3 at. of peroxide of iron is in all probability derived from the water, the hydrogen of which has apparently an action on the lactic acid. By boiling and evaporating in the air the peroxide of iron does not separate; hence we may infer that the product of decomposition from the action of the hydrogen on the lactic acid undergoes a still further change with the oxygen of the air, and forms with the oxide of iron a compound which remains soluble.

(*b*) On exhausting the extract, obtained by evaporating the solution of impure lactate of soda to dryness, with alcohol, only the lactate of soda is dissolved, the caseous matter remaining behind. From the alcoholic solution sulphuric acid precipitates the soda as sulphate. 1 At. of crystallized carbonate of soda of an atomic weight 1790, (the base of which is contained in 1 at. lactate soda), corresponds to 1 at. or 613 parts of concentrated sulphuric acid, so we require of conc. sulphuric acid $\frac{1}{3}$ the weight of the soda used. To re-obtain the alcohol, the solution of lactic acid, previous to distillation is mixed with a moderate quantity of water. By dissolving iron in the residual acid liquid, water is decomposed, the oxygen forms with iron protoxide of the latter, and hydrogen is evolved. The quantity of iron ordered is more than necessary to saturate all the acid present. On account of the high state of dilution in which the acid exists, (but which is necessary for the retention of the lactate of iron in solution even whilst hot) the common iron filings are too coarse to be used. To obtain a good yield of salt it is necessary to filter at the proper time; so soon as no more free lactic acid exists, and consequently no more free hydrogen is eliminated, the protoxide begins to pass over into the state of magnetic oxide, the salt of which is uncrystallizable, and remains as a syrup in the last liquor; (*Vide supra*).

Properties.—Proto-lactate of iron when pure, forms white crystalline crusts or grains, having a tinge of green, and when strongly magnified appearing as adherent masses of rectangular prisms, dissolving with difficulty in water, and possessing a mild sweetish ferruginous taste. 1 Part is soluble in 12 of boiling and 48 parts of cold water. The solutions have a slightly yellowish-green colour, and faint acid reaction. The changes which a lengthened action of heat and air produce, have been explained. Dilute alcohol dissolves a small

quantity, strong alcohol, none of the salt. Heated in a platina spoon, it froths up; gives out a thick white smoke of an acid reaction, and smelling like burning cream of tartar; it then becomes black and finally leaves pure peroxide of iron. The salt may be contaminated with *extractive* and *caseous matter;* in the first place it is of a dirty-grey colour, and in the second yields a residue, on solution in water. A mixture of *protosulphate of iron and sugar of milk*, is known by its giving with an aqueous solution of chloride of barium a dense white precipitate (sulphate of baryta), and if the powder is boiled for ¼ of an hour with nitric acid spec. grav. 1·20 and allowed to cool, a white granular crystalline precipitate separates, which by long standing continually increases, and even with a large quantity of water only partially disappears again. This body is the acid of sugar of milk (mucic acid = $C_6H_4O_7$ + HO) and is formed by the oxidizing action of nitric acid on the sugar of milk ($C_{12}H_{10}O_{10}$):

1 at. $C_{12}H_{10}O_{10}$, and 2 at. NO_5, form
2 at. $C_6H_4O_7$ + HO, and 2 at. NO_2 (which is evolved).

FERRUM PROTOXIDATUM ET PEROXIDATUM PHOSPHORICUM.

Ferri Phosphas.—Blue Phosphate of Proto- and Peroxide of Iron.

FORMULA:
$(3FeO + P_2O_5 + 8HO) + x(3Fe_2O_3 + 2P_2O_5 + 16HO.)$

Preparation.—10 Parts of freshly prepared protosulphate of iron are dissolved in 100 parts of water and mixed with a solution of 13 parts of phosphate of soda in 130 parts of water; (both solutions must be cold); the supernatant liquor is poured off when

the precipitate has subsided, the latter washed with cold water, thrown on a filter, drained on several layers of blotting paper, and dried in the open air (if possible by the sun); the dry precipitate is rubbed to powder and kept in a cool place. The yield is about 5 parts.

Recapitulation.—When solutions of ordinary phosphate of soda and proto-sulphate of iron are mixed together, a white precipitate is formed, which, so long as the proto-sulphate of iron is in excess, is a hydrated tribasic phosphate of protoxide of iron $=3FeO+P_2O_5+8HO$. This precipitate acquires almost directly after its formation a bluish-gray shade, which by washing becomes somewhat stronger, and exposed to the air the precipitate becomes as it dries blue throughout. If, on the other hand, an excess of phosphate of soda is used, it is not, under similar circumstances, of a pure blue tint when dry, but has a tinge of grey, or sometimes a greenish-grey colour. In such a precipitate, we find the proportion of iron to phosphoric acid is not 3 to 1, but 19 to 6, or 16 to 5; that is, the iron predominates. But even the precipitate obtained by excess of proto-sulphate of iron, and equally carefully dried, will be of a dirty-blue colour if the supernatant liquor is not poured off the precipitate so soon as it is thrown down. This liquid, which contains protosalt of iron, soon begins to change, and the proto-phosphate of iron is raised to a perphosphate $=Fe_2O_3+P_2O_5+8HO$, which precipitates. If the proto-sulphate of iron is old, and partially oxidized, the preparation, even with the greatest precaution, will be grayish-green instead of blue.

By following the directions previously given, a preparation of a beautiful blue colour may with certainty be obtained. Several experiments as to the most suitable proportions for the proto-sulphate of iron and phosphate of soda have satisfied me that 2 at. of the former to 1 at. of the latter should

be used. The precipitate contains $\frac{3}{4}$ of the iron of the sulphate, and $\frac{1}{2}$ of the acid of the soda salt, or,

4 at. $FeO + SO_3 + 7HO$, and 2 at. $2NaO + HO + P_2O_5 + 24Aq.$, give about
1 at. $3FeO + P_2O_5 + 8HO$, as a precipitate.

Consequently, 6950 parts of proto-sulphate of iron require 8984 parts of crystallized phosphate of soda. The precipitate weighs 3150 (or 10 parts of proto-sulphate of iron yield 4·5 parts of precipitate), rather more than this is generally obtained, as during the drying in the air a certain portion is converted into peroxide :

2 at. $3FeO + P_2O_5 + 8HO$, and 3 at. O, give
1 at. $3Fe_2O_3 + 2P_2O_5 + 16HO$;

whilst at the same time the blue colour of the precipitate is changed.

The quantity of persalt present is never constant, it varies from 1 in 4 at., to 1 in 9 at. of proto-phosphate, without the colour of the compound being sensibly affected.

When from 4 at. of proto-sulphate of iron, and 2 at. of phosphate of soda, the compound, $3FeO + P_2O_5 + 8HO$ has precipitated, there remains in the solution 1 at. protoxide of iron, 4 at. of soda, 4 at. of sulphuric acid, and 1 at. phosphoric acid. As before stated, this becomes turbid in the air, from oxidation, and deposits $Fe_2O_3 + P_2O_5 + 8HO$; as 1 at. FeO yields only $\frac{1}{2}$ at. of peroxide, the precipitate, when thus iron is thrown down, always contains $\frac{1}{2}$ at. of phosphoric acid, besides the 4 at. of soda and sulphuric acid. It requires, however, a great length of time for the whole of the phosphate of iron to deposit, and it is consequently better to saturate the liquid with lime, and use it for Glauber's salts.

Properties.—Proto-phosphate of iron thus prepared, is a beautiful lavender-blue, odourless, and tasteless

powder. When exposed to a moderate warmth, it instantly loses its blue colour, becoming a greenish-gray; more strongly heated, the water is given off, the proto- is converted into persalt, and the residue is a grayish-brown. It quickly dissolves in hydrochloric acid to a greenish-yellow colour; in the solution ferridcyanide of potassium readily detects the *protoxide of iron* by its blue precipitate, and sulphocyanide of potassium the *peroxide*, from its blood-red colour. If the hydrochloric solution is thrown down by excess of ammonia, the supernatant liquid must be colourless; a blue colour would denote *copper*.

FERRUM PROTOXIDATUM SULPHURICUM.

Ferri Sulphas.—Vitriolum Martis.—Protosulphate of Iron.—Green Vitriol.

FORMULA: $FeO + SO_3 + HO + 6Aq$.

Preparation.—In a glass flask, or, on the large scale, in a leaden vessel, are mixed 6 parts of concentrated sulphuric acid with 24 parts of water, and 4 parts of pure iron turnings or filings; the whole, frequently stirred with a porcelain or wooden spatula, is allowed to digest for one day; the vessel is now placed on the fire, and heated as long as any gas is evolved, then filtered, the hot filtrate mixed with $\frac{1}{4}$ part of concentrated sulphuric acid, and allowed to stand two days in a cool spot. The crystals which have formed, are freed from the mother liquor, and spread out on paper (if possible in the sun) to dry; then kept in a bottle or stone jar. The solution yields, on concentration, a considerable portion of salt, and generally from the above proportion of ingredients, 17 parts of protosulphate are obtained.

Instead of pure sulphuric acid, the residue from

the manufacture of ether may be economically used; but of course a larger quantity of this is necessary. Generally, 10 parts of the ether residue may be considered equal to 6 parts of concentrated sulphuric acid; but care must always be taken that after the evolution of gas is ended, that is, when all the acid has combined with the iron, the latter is still in excess.

Recapitulation.—Concentrated sulphuric acid has no action on iron in the cold, but mixed with a certain portion of water, a lively effervescence ensues; the oxygen is separated from a part of the water and unites with the iron, the proto-oxide of iron thus formed combines with the sulphuric acid, and the hydrogen escapes:

1 at. Fe, 1 at. SO_3, and 1 at. HO, form
1 at. $FeO + SO_3$, and 1 at. H.

In order to dissolve 350 parts of iron, independently of the water necessary for its dilution, 613 parts of monohydrated sulphuric acid are necessary. In the proportion previously given, of 6 parts acid and 4 of iron, we have an excess of the latter; this is rather advantageous than otherwise, as it prevents the solution of any traces of copper that may exist with the iron. Most of the iron dissolves in the cold, and it is only towards the end that the action is to be assisted by warming. Besides the excess of iron (which after the filtration may be washed with water, and quickly dried), there remains on the filter carbonaceous matter, and a little silica. Even the best iron contains a little carbon, which is partly in chemical combination, and partly a mechanical admixture; the latter separates in black flakes, but the former at the moment of its liberation combines with hydrogen, and is given off as the highest carburetted hydrogen (Marsh Gas $= CH_2$), imparting to the hydrogen its unpleasant odour. The quantity of carburetted hydrogen which separates is consi-

derable, if, instead of pure sulphuric acid, the ether residue is employed, for the latter contains a carbonaceous matter in solution (to this it is indebted for its brownish colour), which, yielding up its carbon to the hydrogen, causes at the same time an entire decolorization of the acid. If traces of phosphorus and sulphur are present, the evolved gases are not free from phosphuretted and sulphuretted hydrogen, and have then a nauseous smell. The solution when filtered clear, and previous to crystallization, is, whilst still warm, mixed with some sulphuric acid, which prevents its higher oxidation; the free acid becoming in a certain degree a protecting cover to the salt.

Properties.—Pure proto-sulphate of iron crystallizes in bluish-green oblique rhombic prisms, is odourless, and possesses at first a saline, then a sweetish, astringent taste. At the ordinary temperature it requires scarcely 2 parts of water for its solution, of hot water still less; the solutions have an acid reaction. In alcohol it is insoluble. Exposed to the air, the crystals lose 6 at. of water, and become covered with a white powder $= FeO + SO_3 + HO$, which, from the absorption of oxygen, gradually changes to yellow, loses another atom of water, and forms sesqui-sulphate of peroxide of iron.

2 at. $FeO + SO_3 + HO$, and 1 at. O, form
1 at. $Fe_2O_3 + 2SO_3 + HO = (Fe_2O_3 + SO_3) + (SO_3 + HO)$, and 1 at. HO.

Such a partially-oxidized salt dissolved in water separates into neutral sulphate $= Fe_2O_3 + 3SO_3$, which remains in solution, and into the basic salt $= 2Fe_2O_3 + 3SO_3$, 8HO, which precipitates as a yellowish-brown powder:

3 at. $Fe_2O_3 + 2SO_3 + HO$, and 5 at. HO, form
1 at. $Fe_2O_3 + 3SO_3$, and 1 at. $2Fe_2O_3 + 3SO_3 + 8HO$.

The same yellowish-brown powder precipitates from a solution of proto-sulphate of iron when exposed to the air, whilst the solution becomes at the same time of a yellow colour, and contains peroxide. When heated, proto-sulphate of iron fuses in its water of crystallization, leaving a white powder, which heated more strongly in the air, absorbs oxygen, and becomes red; heated gradually to redness, it evolves sulphuric acid, water, and sulphurous acid, whilst a dark crimson-red powder of pure peroxide of iron remains. The separation of sulphurous acid is occasioned by the decomposition of the sulphuric acid of part of the salt, which as such, is not separable from the protoxide of iron, but the latter combining with 1 at. of its oxygen forms peroxide, and the sulphurous acid then is given off:

2 at. $FeO + SO_3$, forms
1 at. Fe_2O_3, 1 at. SO_2, and 1 at. SO_3.

Any contamination of proto-sulphate of iron with *persulphate*, is known by the grey or greenish-yellow colour of the crystals, and chemically by means of sulphocyanide of potassium, (*Vide* FERRUM CHLORATUM); *oxide of copper* is detected by ammonia. The commercial salt, from iron pyrites is generally contaminated with *oxide of zinc* and *magnesia*. Oxide of zinc is detected by heating the sulphate of iron with nitric acid, adding excess of solution of caustic potash, after a short time heating, filtering, and dropping hydrosulphate of ammonia into the filtrate; if zinc is present, this will cause a white precipitate, insoluble in acetic acid. The caustic potash precipitates the peroxide of iron, oxide of copper and magnesia, and also at first the zinc, but the latter is dissolved in excess of the precipitant. If on treating the solution with acetic acid it partially or entirely disappears, *alumina* is present, in which case the acetic acid solution is rendered turbid by

excess of ammonia. This treatment of the protosulphate with nitric acid, as has been previously related, is to convert it into peroxide, as only the latter is entirely precipitated by potash. To detect the magnesia, all the metals, and any alumina that may be present, are thrown down by hydrosulphate of ammonia, and phosphate of soda added to the filtrate, (*Vide* AMMON. CHLORATUM); should oxalate of ammonia also cause a precipitate, *lime* is present, and must be removed previously to testing with phosphate of soda.

FERRUM SULPHURATUM.

Ferri Sulphidum.—Sulphuret of Iron.

FORMULA: FeS.

Preparation.—6 Parts of iron filings and 4 parts of powdered sulphur are placed in a black lead crucible, which must be only half filled, in alternate layers of sulphur and iron, about $\frac{1}{3}$ of an inch thick, taking care that the latter is on the top; the crucible is covered, the lid fastened on with a wire, and excepting a small opening well luted with clay. As soon as this is dry, the crucible is set on a tile in a good wind furnace, a gentle fire applied at first, but when no more fumes of sulphur escape from the opening of the crucible, gradually increased to a red heat, and continued for at least half-an-hour at this temperature. When quite cold, the contents of the crucible are powdered, and kept in a closed vessel in a dry place. The yield is about 9 parts.

Sulphuret of iron is sometimes prepared by converting 6 parts of iron filings and $3\frac{1}{2}$ parts of sulphur with water into a paste, and evaporating the latter with constant stirring to dryness. This preparation has a black appearance, and when treated with acid

evolves a considerable quantity of gas, which is however little more than pure hydrogen, as in the above process there is formed on the surface of each grain of iron only a thin crust of sulphuret of iron, whilst the interior remains in the metallic state.

Recapitulation.—Iron and sulphur combine at a red heat to simple sulphuret, any excess of sulphur being given off, and coming in contact with the air, ignites, and forms sulphurous acid = SO_2 :

1 at. Fe and 1 at. S, form
1 at. FeS.

350 Parts of iron really require only 200 parts of sulphur, but an excess of the latter is always necessary, as, before the combination of the two is complete, a portion has been volatilized. Practice has shown that there is no better method of preparing it than by placing the two ingredients unmixed in thin layers on each other. After heating, the crucible must not be opened until quite cool, otherwise the mass absorbs oxygen with avidity, becoming partly converted into protosulphate of iron.

Properties —Sulphuret of iron thus prepared is a heavy dark-grey mass, full of blisters, of a partly metallic lustre, odourless, and tasteless. Kept in a closed vessel it undergoes no change, on the other hand, in the air, especially if moist, it oxidizes, and acquires an inky taste. In dilute sulphuric or hydrochloric acid it must, with a powerful evolution of sulphuretted hydrogen gas, gradually and almost entirely dissolve (a thorough solution is not to be expected, on account of the carbon in the iron), and the gas must be entirely absorbed by a solution of acetate of lead ; if this is not the case the gas will contain free hydrogen.

FORMYLUM CHLORATUM.

Formyli Chloridum.—Perchloride of Formyl.—Chloroform.

FORMULA: C_2HCl_3.

Preparation.—In a copper or iron still which must be only half-filled, there are put 50 parts of chloride of lime, 100 parts of water, and 3 parts of alcohol of 90 per ct.; all are well stirred together, and the head luted on; with the still is connected a well cooled worm to which is attached a glass receiver, but not air tight, and the still then heated. So soon as the first portion begins to distil all the fire is withdrawn from the furnace, and if the distillation proceeds too rapidly, the head of the still must be cooled with wet cloths. When the product ceases to come over in a continuous stream, the fire is again added; the receiver is to be withdrawn as soon as it contains 8 parts. If the distillate reddens or bleaches blue litmus paper, which is however not generally the case, it is treated with small portions of hydrate of lime and poured into a narrow high cylindrical glass, and when it has separated into two layers of liquid, the upper portion is removed by means of a syphon, or pipette, whilst the under portion is treated with half its weight of powdered anhydrous chloride of calcium, and distilled with a gentle heat to dryness; the distillate to be kept in a well stopped bottle and cool place. The yield will be 2 or $2\frac{1}{2}$ parts.

Recapitulation.—The chloride of lime consists of a mixture of about 50 per ct. hydrate of lime = CaO + HO, 22 per ct. chloride of calcium = CaCl and 28 per ct. of hypochlorite of lime = CaO + ClO; which corresponds to 4 at. hydrate of lime, 1 at. chloride of calcium and 1 at. hypochlorite of lime. These

proportions vary in the commercial article, arising partly from bad preparation in the first place, from age, or not having been kept in well closed vessels. The bleaching properties of chloride of lime, and consequently its value, depend on the hypochlorite of lime it contains. As in the preparation of chloride of lime equal atoms of hypochlorite of lime and chloride of calcium are always formed:

2 at. CaO and 2 at. Cl, form
1 at. CaCl and 1 at. CaO + ClO,

so, in the fresh state, the chloride of lime, let its bleaching powers be what they may, always contains the two chlorides in this proportion. When by long exposure to the air its bleaching properties have become weaker, the chloride of calcium will be found to be increased at the expense of the hypochlorite of lime; it readily attracts moisture from the air passing into a wet slimy mass. These intimations may suffice to explain the chemical constitution of chloride of lime, and the necessity of using it only in its most potent state, in making the present preparation. We will now pass to its action on alcohol.

Anhydrous alcohol consists of $C_4H_6O_2$. In contact with chloride of lime and the necessary amount of water, the action that ensues is due to the hypochlorite of lime; the chloride of calcium is an indifferent body, and the part taken by the hydrate of lime is only a secondary one, to saturate a portion of the products formed. The result teaches, that in chloroform, $=C_2HCl_3$, only the fourth part of the carbon contained in alcohol is retained; from the other three-fourths is formed formic acid, $=C_2HO_3$; and, as the chloroform and formic acid have one and the same radical (C_2H), 2 at. alcohol form 1 at. chloroform and 3 at. formic acid. From the alcohol are separated 8 at. of hydrogen, which are replaced by 3 at. of chlorine, and 5 at. of oxygen, yielding

chloroform and formic acid. The chlorine, as well as the oxygen required for the oxidation of the hydrogen, is furnished by the hypochlorite of lime, the base of which at the same time serves to neutralize the formic acid. 3 At. hypochlorite of lime contain 3 at. of lime, 3 at. of chlorine, and 3 at. of oxygen; the other 10 at. of oxygen yet wanting are furnished by 5 at. more of hypochlorite of lime, which are then converted into chloride of calcium; the following formula will explain this better:—

2 at. $C_4H_6O_2$, and 8 at. $CaO + ClO$, form
1 at. C_2HCl_3, 3 at. $CaO + C_2HO_3$, 5 at. CaCl, and 8 at. HO.

1150 Parts of anhydrous, or 1280 parts of alcohol of 90 per ct., consequently require 7944 parts of pure hypochlorite of lime, or 28371 parts of chloride of lime of the above composition, and form 1492 parts of chloroform; or, 1 part of alcohol, 90 per ct., requires at least 22 parts of chloride of lime, and forms 1 part of chloroform. Some experiments I have made show, however, that when to 22 parts of chloride of lime only 1 part of alcohol is taken, a considerable quantity of chloride of lime is lost, as from the action of the heat some of the alcohol volatilizes unacted on; in consequence of this, 3 parts of alcohol are ordered to 50 parts of chloride of lime. Should the mixture contain an excess of hypochlorite of lime, this has a decomposing action on the formiate of lime; chloride of calcium, carbonate of lime, free carbonic acid, and water, separate.

1 at. $CaO + C_2HO_3$, and 1 at. $CaO + ClO$ form
1 at. CaCl, 1 at. $CaO + CO_2$, 1 at. CO_2, and 1 at. HO.

The carbonic acid unites with the lime present in the mixture in the free state. As regards the operation itself:—so soon as the mixture is heated to

176° Fah., it experiences a very violent reaction, the mass froths up, and would certainly come over if the retort were more than half filled; even when such is the case, this is not quite impossible, and consequently the fire must be immediately withdrawn, and, if necessary, the still head cooled; only when the effervescence has subsided, which is known by the distillate coming over more slowly than at first, may fire be again applied, in order to draw over the remainder of the chloroform. When about two and a half times the volume of the alcohol employed has distilled over, the distillate will contain all the chloroform, and what now passes into the receiver will have a weak watery taste. The distillate consists of two layers, the lower of which is the chloroform, the upper the water containing all excess of alcohol and a trace of chloroform. If several batches of chloroform are to be prepared, this watery portion need not be thrown away, but reserved for the next mixture, to which it is then necessary to add only $2\frac{1}{2}$ parts of alcohol, instead of 3 parts. In order to withdraw any traces of water that may adhere to the chloroform, it is rectified over chloride of calcium. The residue in the still may be treated like that from the manufacture of caustic ammonia, and used for chloride of calcium.

Properties.—Pure chloroform is a transparent, heavy liquid, of an agreeable ethereal smell, and somewhat sweetish flavour; its spec. grav. is 1·49, it boils at 142° Fah., entirely volatilizes at a gentle heat, has a neutral reaction, does not ignite when a burning substance is brought to it, but burns in the flame of a candle, the summit of which has in consequence a green tint. Water dissolves but a very small portion of it, sufficient, however, to acquire its taste and smell; with alcohol and ether it is mixible in every proportion, and these mixtures readily ignite. With a solution of nitrate of silver

it causes no turbidness. Mixed with concentrated sulphuric acid, the latter subsides without affecting its colour or otherwise changing it; on the other hand, chloroform sinks to the bottom of a mixture of equal parts sulphuric acid and water. Potassium and hydrate of potash exert no action on it. With an alcoholic solution of potash it is decomposed, in the cold slowly, but when heated more rapidly, into formiate of potash and chloride of potassium:

1 at. C_2HCl_3, and 4 at. KO, form
1 at. $KO + C_2HO_3$, and 3 at. KCl.

From these properties the purity of chloroform may readily be judged. In testing, especial notice must be taken of its spec. grav.; if less than 1·49 it contains a mixture of *lighter fluids* (alcohol, ether, or aldehyde), and in this case, on applying a flame to the vapour, it ignites, and the volume of such a mixture sensibly diminishes when shaken with twice its bulk of pure water. If it reddens litmus paper, it contains free *hydrochloric acid*, and nitrate of silver causes in it a white precipitate of chloride of silver insoluble in water; if free *chlorine* is present litmus paper will be bleached and a precipitate also caused with nitrate of silver solution. If the chloroform has an acid reaction, and nitrate of silver causes in it no precipitate, or one soluble in a quantity of water, *acetic acid* is present, owing to the transformation of aldehyde, with which it was contaminated, in the air.

FORMYLUM IODATUM.

Formyli Iodidum.—Iodide of Formyle.—Iodoform.

FORMULA: C_2HI_3.

Preparation.—2 Parts of carbonate of potash, 2 parts of iodine, 1 part of alcohol of 90 per ct., and 5 parts of water are put into a retort, the latter placed in a water bath after attaching a receiver, and heated until its liquid contents are entirely colourless. A sand bath may be used, but in this care must be taken that the temperature is not more than sufficient to keep up the most gentle evolution of gas; the receiver must, during the operation, be well cooled. When the retort is quite cool its contents are poured into the receiver, the latter emptied into a cylindrical glass, and allowed to subside; the mass of yellow scales are collected on a filter, well washed with water, and dried by pressing several times between filtering paper. The yield is about 17 per ct. or $\frac{1}{6}$ the weight of the iodine used.

Recapitulation.—The mutual action of the carbonate of potash (dissolved in the water) iodine and alcohol is very complicated, including several distinct and, in themselves, by no means simple processes, which, in order to obtain a clear idea and satisfactory explanation as to the small yield of iodoform in proportion to the iodine employed, must be considered separately. We have to bear in mind (1st) the mutual action of carbonate of potash and iodine; (2nd) that of iodine and alcohol; (3rd) that of carbonate of potash, iodine, and alcohol.

(1)—*Carbonate of Potash and Iodine.*—Iodine is soluble in a considerable proportion in a solution of carbonate of potash; but, at the same time, there is very little or no chemical action, according to the

generally received notion; this, however, I have satisfied myself is an error, as it forms, with evolution of carbonic acid, iodide of potassium and iodate of potash, just as if caustic potash had been used:

6 at. $KO + CO_2$, and 6 at. I, form
5 at. KI, 1 at. $KO + IO_5$, and 6 at. CO_2.

The complete conversion of the iodine into these two salts is, however, much slower than with pure potash, with which the combination is instantaneous.*

(2)—*Iodine and Alcohol.*—We know that tincture of iodine always contains, after long standing, hydriodic acid, iodic ether, and probably many other products. This decomposition occurs at a higher temperature much more quickly and decidedly, and the hydriodic acid acts on the carbonate of potash, if this is present, forming iodide of potassium.

(3)—*Carbonate of Potash, Iodine, and Alcohol.*—From these three substances in contact with each other, iodoform results. Without taking into consideration the foregoing processes, which, as has been stated, always accompany the formation of the iodoform, it finally happens, that the oxygen from 5 at. of potash unites itself with 1 at. of alcohol, $= C_1H_6O_2$, causing the formation of 1 at. of formic acid (which combines with another atom of potash)

* The experiments I have made are as follows:—10 gr. of carbonate of potash, 20 gr. of iodine, and 30 gr. of water, after digestion in the warm for two hours, were not decolorized; on cooling, the solution deposited some grains of iodate of potash; evaporated to dryness, heated to redness with charcoal, and again dissolved in water, I obtained a liquid with a powerful alkaline re-action, which, supersaturated with acetic acid, gave off very few gas bubbles, and, precipitated with nitrate of silver, yielded 27·30 gr. of iodide of silver, which correspond to 14·717 of iodine and 8·046 gr. of carbonate of potash. Consequently, of the 10 gr. of carbonate of potash, more than 8 gr. or 4-5ths were converted into iodide of potassium and iodate of potash. When 20 gr. of iodine and 20 gr. of carbonate of potash were taken the decolorization was complete after a digestion of 3 hours, very little of the iodine being volatilized, as I obtained in the above method 36·28 gr. of iodide of silver = 19·60 gr. iodine.

and 4 at. of water; the 5 at. of potassium thus liberated, unite with 5 at. of iodine to form iodide of potassium, and the C_2H of the alcohol, remaining after the separation of the formic acid form with 3 at. iodine iodoform. The carbonic acid of the carbonate of potash is given off.

6 at. $KO + CO_2$, 8 at. I, and 1 at. $C_4H_6O_2$, form
1 at. $KO + C_3HO_2$, 5 at. KI, 1 at. C_2HI_3, 4 at. HO, and 6 at. CO_2.

We find, that for 12688 parts of iodine are required 5190 parts of carbonate of potash, and 575 parts of anhydrous, or 640 of alcohol, of 90 per ct.; and the yield of iodoform should be at least 38 per ct. of the weight of the iodine employed, if the reaction was a simple one. The other transformations must, however, be taken into account, and the alcohol also be used in rather larger proportion, as part of it volatilizes during the digestion. The considerable excess of carbonate of potash appears to cause no decomposition or other evil result to the iodoform, but rather to promote its formation. The operation can scarcely be performed in an open flask, as before all the iodoform is formed, a portion volatilizes, and either condenses in the neck of the retort, or passes over with some of the liquid into the receiver. If the iodoform is not sufficiently washed, iodate of potash will remain mixed with it. On account of the ready volatility of the iodoform, it is better to dry it in the manner directed.

The liquid filtered from the iodoform, which, besides traces of this body, contains all the iodine as iodate of potash and iodide of potassium, together with formiate and carbonate of potash, may be used for making iodide of potassium. For this purpose, it is evaporated to dryness, the saline residue rubbed up with $\frac{1}{8}$th its weight of powdered wood charcoal (*vide* POTASSIUM IODATUM), heated to redness for a

short time in an iron crucible, digested with alcohol, filtered, and the solution evaporated to crystallization. By this means none of the iodine is lost, being obtained either as iodide of potassium, or iodoform.

Properties.—Iodoform forms lemon-yellow laminated scales, which magnified appear more or less as six-sided plates; it is soft to the touch, and of an aromatic smell, like saffron, or rather, perhaps, like a mixture of iodine and chloroform; its taste is similar, but becoming disagreeably strong of iodine; it volatilizes slightly at the ordinary temperature, at 212° Fah. quickly and without decomposition (consequently it is readily drawn over with water), fuses at 240° Fah.—248° Fah. to a brown liquid, but with partial decomposition into iodine vapour, iodureted hydrogen and residual carbon, which, strongly heated in the air, leaves no residue. Water shaken with iodoform acquires, in a very slight degree, its odour and taste, it dissolves only $\frac{1}{1300}$ part; on the other hand, 1 part of iodoform is soluble in 80 parts of cold, and in 12 parts of boiling alcohol, of 80 per ct., and still more readily in boiling ether. The alcoholic solution varies from a straw colour to sulphur-yellow, the ethereal is golden-yellow; both solutions have a neutral reaction, with a sweetish ethereal taste, but afterwards a continuous burning one of iodine. Aqueous solution of potash, when warm, has no action on iodoform, whilst an alcoholic solution quickly decomposes it into formiate of potash and iodide of potassium:—

1 at. C_2HI_3, and 4 at. KO, form
1 at. $KO + C_2HO_3$, and 3 at. KI.

HYDRARGYRUM PURUM.

Pure Mercury.—Quicksilver.

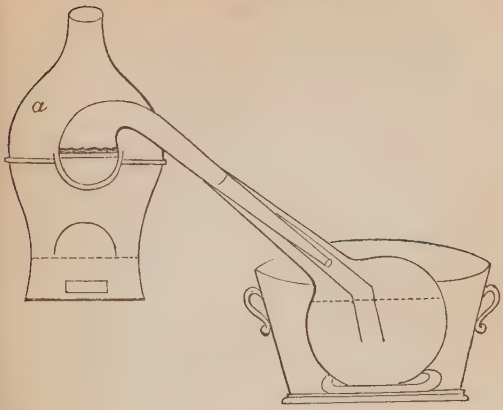
FORMULA: Hg.

Purification.—Of all the methods which have been proposed for the purification of quicksilver, that by distillation is the shortest and best. When there is no haste, concentrated sulphuric acid may with advantage be used.

(*a*)—*By distillation.*—A small, plain retort, of strong glass, is half filled with 12 parts of commercial quicksilver, mixed with 1 part of clean iron turnings, the retort is placed in a deep iron pot, the space between this and the retort filled with sand, the pot placed upon an iron ring, some inches above the surface of the fire, in a furnace with a good draught. The retort is inclined as much as possible, and lengthened to 6 or 8 inches with a cylinder of writing paper, which however must not fit closely to the beak of the retort, but allow a small empty space between the glass and paper. A flask of strong glass is now filled, almost to the neck, with water, and attached without any luting, so that about half the paper cylinder is under water; the flask rests on a little straw, in a vessel filled with water. It requires no further cooling. The accompanying drawing will better explain the apparatus:—

When all this is arranged, fire is applied, at first gently, the heat is then gradually increased, and the draught assisted by a chimney of earthenware or sheet iron, placed on the top of the furnace.* The quicksilver soon boils, and volatilizes with a gentle bubbling; the vapours condense in the upper

* This is supposing that an open charcoal furnace, unconnected with any flue, is used. With ordinary furnaces this is obviously unnecessary.



part of the retort neck, in globules, which rolling down collect under the water. When no more globules appear in the retort neck, the fire is allowed to go out. After cooling, the water is poured from the mercury, the thin pellicle of oxide of iron and oxide of mercury, which generally covers it, is removed by hydrochloric acid, and then washed several times with pure water; by gently warming, any adherent water is driven off. To remove any threads from paper or other impurities, it is run through a cone of writing paper, having a fine hole, made with a pin, at the point; it is then kept in a closed vessel.

To carry on the distillation readily and with safety, not more than three pounds of quicksilver should be operated on at once. If larger quantities are purified in this manner, the second quantity is poured on the iron remaining from the first distillation; the same with the third portion, and so on.

(*b*)—*By treating with concentrated sulphuric acid.*—The mercury is poured into a very flat porcelain dish, so as to expose a large surface, about its volume of concentrated sulphuric acid is then poured on it, and, frequently agitating with a glass rod, it is allowed to digest for a week, at the ordinary temperature. If, after this time, no smell of sulphurous acid gas has been evolved, nor the acid become turbid, it is poured off, the metal well washed with pure water, dried and filtered (as under (*a*)) through a paper cone. If the acid has become turbid, about an ounce of metal is taken out, washed, and digested with a fresh portion of acid, for several days; should it now remain clear and evolve no sulphurous acid, it denotes that the metal was thoroughly purified by the first operation; it is then washed, &c. If, however, the acid has an action on the metal, the whole quantity is allowed to digest one week longer, in contact with the same acid, a second test portion is then withdrawn, and treated as the first.

There are two other methods of purifying quicksilver, which, however, I cannot recommend. The first of these, by agitation with a solution of *bichloride of mercury*, is grounded on theoretical presumptions, which practice does not substantiate. The bichloride of mercury should give up its chlorine to the foreign metals, rendering them soluble, and becoming reduced itself to the metallic state; this is, however, not the case, as the bichloride combines with more mercury, forming calomel, and, by continued agitation, all the mercury is converted into a gray powder. The second method consists in shaking with dilute nitric acid, or solution of pernitrate of mercury, and is imperfect, as the foreign metals can only be entirely removed when a portion of the quicksilver remains dissolved, *i.e.*, when a considerable excess of the purifier has been used.

Recapitulation.—(*a*) By distillation of the mercury, all the foreign metals are found in the residue. On account of the great pressure which mercury exerts on the sides of the retort, this must not be chosen too thin. The use of the iron turnings is, by affording a number of points, to prevent any bumping during the boiling of the mercury. The cylinder of paper which conducts the globules of mercury directly into the water, must not fit entirely air tight on the neck of the retort, otherwise, so soon as the heat lessens, the cold water of the receiver is forced, by the atmospheric pressure, into contact with the hot glass, and cracks it. A small portion of quicksilver vapour combines, during its distillation, with the oxygen of the air in the retort, becoming what is called Mercurius precipitatus per se, whilst a little of the iron filings are carried over at the same time, and oxidized also at the expense of the air and water; these two oxides, form the thin pellicle on the distillate. Particles of dirt adhere to the paper, when filtered through it.

(*b*) At the ordinary temperature pure mercury is not the least acted on by concentrated sulphuric acid, on the other hand all those metals which serve for its adulteration, as lead, zinc, tin, antimony, become oxidized and converted into sulphates, giving to the excess of acid a turbid appearance. The oxidation of these metals takes place at the cost of a portion of the sulphuric acid which is reduced to sulphurous acid, and thus evolved. At first sight we should expect that the lead would undergo no change, this metal not being acted on when concentrated sulphuric acid is poured over it; there are however two conditions favourable to its oxidation to be taken into consideration; in the first place, the lead amalgamated with mercury is in a very high state of division; and secondly, the electrical opposition between the sulphuric acid and lead is in-

creased owing to the presence of the mercury, and at the same time their combining power is increased. Metals, as cadmium and bismuth which are removeable in the same manner, are on account of their high price scarcely ever found as adulterations in commercial quicksilver. Others which amalgamate with mercury as silver, gold, and platinum, not being acted on by sulphuric acid are separated only by distillation.

Properties.—Pure mercury is a silver-white fluid with a tinge of grey, of a powerful lustre, odourless and tasteless, of a spec. grav. 13·5. It is slightly volatile even at the ordinary temperature; when boiled it should pass off without leaving a residue. It is dissolved by nitric acid at the ordinary temperature; by sulphuric only when heated with concentrated acid; hydrochloric acid neither dissolves nor acts on it. Kept in closed vessels it undergoes no change, neither does it in pure air. When it is exposed for any length of time to an atmosphere of sulphuretted hydrogen, it becomes covered with a grey or black coating, which is sulphuret of mercury. Its purity is known by the brightness of its lustre and fluidity, its leaving no scum when poured from a vessel, and no residue on heating a small portion in a retort to redness. If there is a residue, the retort is broken to obtain it uncontaminated with mercury, of which there are generally small portions adhering to the neck, a portion of it digested with hydrochloric acid, the solution poured off the insoluble residue, and treated with solution of chloride of gold; should this cause a grey or purple-coloured turbidness, *tin* is present; (*Vide* Acid Muriat.). The other portion of the residue is treated with nitric acid and warmed; should a white precipitate form, it doubtless arises from *tin* or *antimony*, or both, these metals being oxidized but not dissolved by nitric acid; should the hydrochloric acid have dissolved no tin

this will be oxide of antimony; to determine this a small portion of the washed and dried precipitate is heated on charcoal in the outer flame of the blow-pipe; the oxide of antimony is dissipated and partially condenses on the cool part of the charcoal as a white precipitate, whilst the oxide of tin remains unaltered. If the nitric acid solution gives a white precipitate with sulphate of soda it denotes the presence of *lead;* when the sulphate of lead is filtered off, and the last trace of lead removed by sulphuretted hydrogen, should the clear solution neutralized with ammonia give with sulphide of ammonium a white precipitate, *zinc* is present. *Iron* and *copper*, which can however exist only in minute portions, may be detected in the nitric acid solution, the first by the red colour it gives with sulphocyanide of potassium, (*vide* FERRUM. CHLORAT.), the second by its blue solution with excess of ammonia.

HYDRARGYRUM BROMATUM.

Hydrargyri Bromidum.—Proto-bromide of Mercury.

FORMULA: Hg_2Br.

Preparation.—8 Parts of dry proto-nitrate of mercury (*vide* HYDRARG. PROTO-NITR.) are rubbed in a porcelain mortar with 16 parts of pure water and 1 part of nitric acid, spec. grav. 1·2, then 60 parts of pure water gradually added, the whole warmed in a glass flask until entirely dissolved, filtered if necessary, the solution diluted with eight times its weight of water, and a solution of bromide of potassium added as long as it causes a precipitate. 4 Parts of bromide of potassium will be requisite. The precipitate is collected on a filter in a dark place, thoroughly washed (until the wash water has no longer an acid reaction nor leaves a residue on

evaporation), dried, and kept in a bottle excluded from the light. It will weigh nearly eight parts.

From perbromide of mercury the proto-bromide may be prepared in the dry way as in making calomel; (*Vide* HYDRARG. PROTOCHLOR.). $2\frac{1}{4}$ Parts of metallic quicksilver are used, instead of 3 parts, for 4 parts of bromide.

Recapitulation.—To dissolve the proto-nitrate thoroughly in a large amount of water the addition of a certain amount of free nitric acid is necessary, otherwise it becomes partially decomposed; (*Vide* HYDRARG. PROTO-NITR.) Bromide of potassium throws down proto-bromide of mercury from this solution, whilst the potassium acquiring the oxygen of the protoxide of mercury combines with the nitric acid; the saltpetre thus formed remaining dissolved.

1 at. $Hg_2O + NO_5 + 2HO$, and 1 at. KBr, form
1 at. Hg_2Br, 1 at. $KO + NO_5$, and 2 at. HO.

3500 Parts of protosalt of mercury require 1490 parts of bromide of potassium. The collecting, washing, and drying the precipitate must be carried on in a dark place, or, as with all other salts of mercury, it is partly reduced and becomes grey.

Properties.—Both the sublimed and precipitated proto-bromide of mercury so much resemble their analogous compounds with chlorine, calomel, that what is said of one holds good for the other. The bromide is distinguishable from the chloride by its reaction with chromate of potash and sulphuric acid. On distilling the bromide with half its weight of chromate of potash, and rather more than its weight of concentrated sulphuric acid, a reddish-brown gas is evolved, which is pure bromine, and becomes colourless when shaken with caustic potash solution. The residue in the retort consists of persulphate of mercury, sulphate of chrome, and bisulphate of potash.

3 at. Hg_2Br, $4KO + CrO_3$, and 20 at. $SO_3 + HO$, form
6 at. $HgO + SO_3$, 2 at. $Cr_2O_3 + 3SO_3$, 4 at. $KO + SO_3 + HO + SO_3$, 16 at. HO, and 3 at. Br.

On agitating the distillate with solution of potash, bromate of potash and bromide of potassium are formed.

6 at. KO, and 6 at. Br, form
1 at. $KO + BrO_5$, and 5 at. KBr.

The above test causes, with chloride of mercury, no evolution of pure chlorine, but chromate of chloride of chrome $= 2CrO_3 + CrCl_3$, which agitated with caustic potash solution retains a yellow colour;

3 at. Hg_2Cl, 5 at. $KO + CrO_3$, and 19 at. $SO_3 + HO$, form
6 at. $HgO + SO_3$, 1 at. $Cr_2O_3 + 3SO_3$, 5 at. $(KO + SO_3) + (HO + SO_3)$, 14 at. HO, and 1 at. $2CrO_3 + CrCl_3$.

Caustic potash solution converts the latter compound into chloride of potassium and yellow chromate of potash.

1 at. $2CrO_3 + CrCl_3$, and 6 at. KO, form
3 at. KCl, and 3 at. $KO + CrO_3$.

HYDRARGYRUM BIBROMATUM.

Hydrargyri Perbromidum.—Perbromide of Mercury.

FORMULA: HgBr.

Preparation.—(a) With Bromine.—To 1 part of mercury and 2 of water, in a porcelain mortar, 1 part of bromine in small portions is gradually added, the whole rubbed together for some time, put into a glass flask, and after the addition of 40 parts of water heated to boiling, filtered when all

but a trifling grey residue is dissolved, and the filtrate still hot placed in a cool spot. After standing a day, the crystals are separated from the mother liquor, the latter evaporated, allowed to crystallize, again evaporated, and this repeated as long as crystals are formed. The crystals are dried with a very moderate warmth, and kept in a vessel, from which light is excluded. The yield is $1\frac{1}{2}$ parts.

(*b*) *With Bromide of Potassium.*—9 Parts of red oxide of mercury are dissolved in a capacious porcelain dish with the smallest possible quantity of nitric acid (17 parts of an acid spec. grav. 1·20 will be enough,) the solution is diluted with water to 40 parts, a previously prepared solution of 10 parts of bromide of potassium in 30 parts of water is added to it, and with constant stirring evaporated to dryness; towards the last with a gentle heat. The dry saline mass, which will weigh about 24 parts, is finely powdered and digested for an hour with four times its weight of alcohol of 80 per ct., filtered whilst hot, the residue washed with some hot alcohol, and the alcoholic solution put in a cold place. After one or two days the crystals which form are separated from the mother liquor, this is concentrated, and so on as long as crystals form. The salt when dried in the air will weigh about 14 parts.

Recapitulation.—(*a*) Bromine combines directly with mercury; but to prevent the action from being too violent they are mixed gradually. The mercury on the gradual addition of the bromine becomes converted (with evolution of heat), first into a grey, (mercury and proto-bromide of mercury $= Hg_2Br$.), then into a white powder which is almost entirely perbromide.

1 at. Hg, and 1 at. Br, form
1 at. Hg.Br.

1250 Parts of mercury should require 1000 parts of anhydrous bromine; rather more of the latter than

this is necessary, as, from the warmth during the combination, a portion volatilizes, a small quantity also remains dissolved in the water present, and does not combine with the mercury. The loss of bromine would of course be more considerable if much water was added to the mercury at first. Without the addition of any water, a much larger portion of bromine would be lost by evaporation. Toward the end of the process, the product is treated with boiling water, partly to obtain it in crystals, partly to separate a small quantity of mercury and proto-bromide of mercury, which, in spite of the excess of bromine, is almost always present. On account of the difficulty with which the bromide dissolves, a good quantity of water is required. The crystals must be kept in a dark place, or, like all other mercurial preparations, they undergo a partial reduction.

(*b*) Oxide of Mercury readily dissolves in moderately dilute nitric acid, and forms pernitrate of mercury :—

1 at. HgO, and 1 at. NO_5, form
1 at. $HgO + NO_5$.

1350 Parts of oxide require 675 parts of anhydrous nitric acid, or 2500 parts of hydrated, of spec. grav. 1·20 (containing 27 per ct. of anhydrous). This solution, in contact with bromide of potassium, yields up the oxygen of the metallic oxide to the potassium, with which the nitric acid forms nitrate of potash ; the mercury uniting with the bromine.

1 at. $HgO + NO_5$, and 1 at. KBr, form
1 at. $KO + NO_5$, and 1 at. $HgBr$.

1350 Parts of oxide of mercury (contained in 1 at. of nitrate) require 1490 parts of bromide of potassium ; as soon as they are mixed, the bromide of mercury, on account of its density, partially precipitates. To render it entirely free from nitrate

of potash it is dried, and exhausted with alcohol, in which the nitre is insoluble.

Properties.—Whichever way the perbromide of mercury is prepared, it forms white, flattened, oblique, rectangular prisms, of a silvery lustre, odourless, but of a nauseous metallic taste. It melts when heated, and volatilizes entirely to a white scaly sublimate. In water it dissolves with difficulty, requiring 250 parts at the ordinary temperature, and 25 parts of boiling water. The cold solution has no action on litmus paper; that for which hot water has been used, gives a slightly acid reaction. At the ordinary temperature, alcohol of 80 per ct. dissolves $\frac{1}{12}$, boiling alcohol $\frac{1}{3}$ of its weight. Ether is a still better solvent. With chromate of potash and sulphuric acid (*vide* the previous article), a falsification with perchloride of mercury is readily detected.

HYDRARGYRUM CHLORATUM.

Hydrargyri Chloridum.—Proto-chloride of Mercury.—Calomel.

FORMULA: Hg_2Cl.

Preparation.—(*a*) *By the dry way.*—4 Parts of bichloride of mercury are reduced, in a porcelain mortar, with a little spirit (to keep down the dust), to a fine powder; 3 parts of metallic mercury are added to it, and the trituration continued until no more mercury globules are visible The gray mixture is put into a flask, which it should only $\frac{1}{3}$ part fill, the latter placed in an iron dish containing a very thin layer of sand, then surrounded with sand to half its depth, the whole put on a ring furnace, and heat applied. For fear of the glass cracking, the fire must not be strong at first, but gradually increased. As soon as the sublimate condenses on

the upper part of the flask, the mouth of the latter is carefully closed, to prevent loss. From time to time the covering is removed, the better to observe the process, and so soon as the bottom of the flask is empty, it is withdrawn from the sand, a wet sponge or cloth applied, in order to crack it, and when thoroughly cool the glass fragments separated from the sublimate, and the latter kept in a bottle, away from the light. The yield will be nearly 7 parts.

(*b*) *By the moist way.*—8 Parts of dry proto-nitrate of mercury are rubbed in a porcelain mortar with 16 parts of pure water, with which 1 part of nitric acid, spec. grav. 1·2, has been mixed; to this about 60 parts of water are gradually added, the whole gently warmed in a glass flask until entirely dissolved, filtered if necessary, the solution diluted with eight times its weight of water, and a solution of common salt added as long as a precipitate is formed; for this nearly 2 parts of salt will be requisite. The precipitate, not exposed to the light more than necessary, is collected on a filter, thoroughly washed with pure water (until the water loses all acid reaction, and a portion of it leaves no residue on evaporation), then dried with a gentle heat and but slight exposure to light. It will weigh $6\frac{1}{2}$ parts.

Sal ammoniac will not serve for this precipitation, as (on account of its tendency to form, with per-chloride of mercury, a readily-soluble double salt) it causes, even in the cold, a partial decomposition of the precipitate (proto-chloride of mercury) into perchloride of mercury and metallic mercury:

1 at. Hg_2Cl, decomposes into
1 at. HgCl, and 1 at. Hg;

thus, not only causing a loss, but also a contamination of the precipitate with finely-divided mercury.

Neither will hydrochloric acid serve for the precipitation, as the liberated nitric acid converts a portion of the precipitate into soluble perchloride and pernitrate of mercury :—

3 at. Hg_2Cl, and 4 at. NO_5, form
3 at. HgCl, 3 at. $HgO + NO_5$, and 1 at. NO_2.

Recapitulation.—(*a*) Perchloride of mercury is capable of taking up another atom of mercury, forming, by this means, an insoluble compound, calomel :—

1 at. HgCl, and 1 at. Hg, give
1 at. Hg_2Cl.

1693 Parts of chloride require 1250 parts of metal. The trifling excess of quicksilver contained in the given proportions, 4 parts and 3 parts, is not disadvantageous, being volatilized before the calomel sublimes, and is so far useful as affording a proof that all the per- is converted into proto-chloride of mercury. The formation of the proto-chloride takes place previous to the sublimation, and is known by the mixture acquiring a lemon-yellow colour. The sublimation requires a tolerably strong and continued heat, and with ordinary precaution is without danger.

(*b*) Proto-nitrate of mercury and chloride of sodium change elements when their aqueous solutions come together, proto-chloride of mercury precipitates, and nitrate of soda remains dissolved :—

1 at. $Hg_2O + NO_5 + 2HO$, and 1 at. NaCl, form
1 at. Hg_2Cl, 1 at. $NaO + NO_5$, and 2 at. HO.

3500 Parts of crystallized proto-nitrate of mercury require 733 parts of chloride of sodium; of the commercial common salt (and this equally answers the purpose) rather more will be requisite, on account of the moisture and impurities it contains. The presence of free nitric acid is necessary, to pre-

vent the composition of the nitrate of mercury from becoming changed when dissolved in a large amount of water; for this purpose, 1 part of acid to 8 parts of salt suffices. The change which pure water occasions in this salt is further treated of under the article HYDRARG. PROTOX. NITRICUM.

Properties.—Sublimed calomel appears as a crystalline crust, consisting of four-sided prisms, of a white colour, with a tinge of yellow, which, on scratching or rubbing, acquire a pale yellow colour; the precipitate is a perfectly white amorphous powder. It is odourless and tasteless; heated, it becomes yellow, and volatilizes without fusing, forming white fumes; by repeated sublimations, it is partially decomposed into perchloride of and metallic mercury. Exposed to the light, it undergoes a similar decomposition, and acquires a gray colour; by a protracted action of the light, the perchloride decomposes, chlorine is evolved, and the mercury with which it was combined remains as a gray powder. Cold water does not dissolve a trace of calomel; hot water decomposes it (but only in a slight degree), into soluble chloride and metal; the water when filtered giving, with sulphide of ammonium, a black precipitate. Alcohol behaves like water, but exerts a still greater decomposing action at its boiling point. Boiled for some time with hydrochloric acid calomel dissolves, hydrogen being evolved, and perchloride of mercury formed:—

1 at. Hg_2Cl, and 1 at. HCl, form
2 at. HgCl, and 1 at. H.

When boiled with nitric acid also, it entirely dissolves, nitric oxide is evolved, and forms, in the air, hyponitric acid. Calomel of a gray colour contains *free mercury*. If cold water which has been agitated with it some time gives, with sulphide of ammonium, a black precipitate, it is not free from

corrosive sublimate (perchloride), which is probably owing to the perchloride and mercury not being sufficiently well mixed previous to their sublimation. In testing calomel for corrosive sublimate, it must not, for reasons previously given, be treated with boiling water. There is no advantage in replacing the water by alcohol or ether, and solution of sal ammoniac is inadmissible.

HYDRARGYRUM BICHLORATUM.

Hydrargyri Perchloridum.—Perchloride of Mercury. —Corrosive Sublimate.

FORMULA: $HgCl_2$.

Preparation.—(*a*) *By the dry way.*—Mix 2 parts of dry neutral persulphate of mercury in a porcelain mortar, intimately with 1 part of powdered and well-dried common salt; shake the mixture into a glass flask, which should only be one-fourth part filled, and sublime as for HYDRARG. CHLORATUM. The heat in this case need not be so great as with calomel, otherwise a considerable portion of the sublimed salt would fuse, and fall back again; thus rather retard than facilitate the process. When no more white stellated groups of crystals appear on the surface of the powder at the bottom of the flask, the latter is withdrawn from the sand, cracked by touching with a wet sponge, and when cold the sublimate in the upper portion of the flask is separated from the glass, and kept in vessels excluded from light. The yield is $1\frac{3}{4}$ parts.

(*b*) *By the moist way.*—At the present low price of hydrochloric and nitric acids, perchloride of mercury may also be advantageously prepared in the following manner:—6 Parts of mercury, 14 parts of hydrochloric acid, spec. grav. 1·130, and 7 parts of nitric acid, spec. grav. 1·20 (the acids need

not be chemically pure, but should they contain sulphuric acid, a little common salt must be added) are mixed in a plain retort, the latter is placed in a sand bath, a receiver attached without luting, and kept cool, whilst the distillation is carried on to dryness. When no more moisture forms in the neck of the retort, the receiver is exchanged for a dry one, the retort is buried as deeply as possible in the sand, and the heat continued until the salt is driven to the upper portion, and into the neck of it. The retort is then withdrawn from the sand, a wet cloth applied to the bottom, when cold the contents separated from the glass, and the product, which will be about 8 parts, kept in a bottle excluded from the light.

Recapitulation.—(*a*) Persulphate of mercury and chloride of sodium when heated together exchange elements, the oxygen of the oxide of mercury passes to the sodium, and the soda thus formed combines with the sulphuric acid; the mercury and chlorine unite and volatilize, whilst sulphate of soda remains behind :—

1 at. $HgO + SO_3$, and 1 at. NaCl, form
1 at. HgCl, and 1 at. $NaO + SO_3$.

1850 Parts of persulphate of mercury require only 733 parts of common salt, rather more than this is contained in the above proportion, 2 parts and 1 part. Common salt, as found in commerce, is not quite pure, and at its low price the loss from a slight excess is very trifling, whilst this insures the more perfect decomposition of the persulphate of mercury, which is especially dependent on the intimate admixture of the salts, but there is no necessity, as is generally stated, to take equal portions of each. In separating the sublimate from the glass, care must be taken that it is not contaminated by the sulphate of soda at the bottom; this, on account of

a trace of sublimate it may contain, must be thrown away.

(*b*) Hydrochloric acid has no action on mercury, either cold or hot; but when nitric acid also is present, aqua regia forms,* and the metal soon dissolves entirely, forming per-chloride of mercury, water, and nitric oxide, which forms, in the air, brown vapours of hyponitric acid, $=NO_4$:—

3 at. Hg, 3 at. HCl, and 1 at. NO_3, form
3 at. HgCl, 3 at. HO, and 1 at. NO_2.

3750 Parts of mercury require 1365 parts of anhydrous, or 5250 of hydrochloric acid of spec. grav. 1·130 (containing 26 per ct. of anhydrous), and 675 parts of anhydrous nitric acid, or 2500 parts, having a spec. grav. 1·20 (=27 per ct. anhydrous acid). In the proportions previously given, the acids are in excess of this, but the loss that occurs during the solution renders it necessary. When most of the liquid has passed over, and the residue acquires a syrupy consistence, the fire must be slackened for a time, otherwise it causes a spurting of the contents. By sublimation the preparation is obtained quite free from all the impurities, which remain behind. The common salt, that is added to retain the sulphuric acid, becomes converted into sulphate of soda; (*Vide* Acid. Muriat.).

Properties.—Bichloride of mercury forms a snow-white crystalline mass, consisting of rhombic prisms heaped together; rubbed up it forms a white powder, is odourless, but possesses an extremely

* When nitric and hydrochloric acids are mixed they mutually decompose into nitric oxide, chlorine, and water:

3 at. ClH, and 1 at. NO_5, form
1 at. NO_2, 3 at. Cl, and 3 at. HO.

More correctly speaking, the nitric oxide at the moment of its liberation combines with 1 or 2 at. of chlorine, leaving only 2 or 1 at. chlorine free; this NO_2Cl or NO_2Cl_2, on coming in contact with a metal, again separates, giving up its chlorine, &c.

nauseous metallic taste; heated it fuses, volatilizing readily and completely. In water, ether, and alcohol, it must be entirely soluble. 1 Part of the salt dissolves in 16 parts of cold and 3 parts of boiling water, $2\frac{1}{2}$ parts of cold alcohol, and 3 parts of ether; all of which solutions have an acid reaction. In the light it becomes reduced, first to proto-chloride, and finally to the metallic state; this change, however, makes but little difference to its weight. If, on treating with water, there is a white residue, blackened by solution of potash, *calomel* is present. The potash abstracts the chlorine from the calomel, and, giving up its own oxygen to the mercury, forms black protoxide:—

1 at. KO, and 1 at. Hg_2Cl, form
1 at. Hg_2O, and 1 at. KCl.

The commercial article sometimes contains red spots, which consist of *peroxide of iron*.

HYDRARGYRUM BICHLORATUM AMMONIATUM.

Hydrargyri Ammonio-Chloridum.—Ammonio Chloride of Mercury.—White Precipitate.

Formula of that thrown down by Ammonia:

$$HgCl + NH_2Hg.$$

Formula of that thrown down by Carbonate of Soda:

$$HgCl + NH_2Hg + 2HO.*$$

Preparation.—(*a*) *With ammonia.*—1 Part of perchloride of mercury is dissolved in 30 parts of

* The composition of this precipitate is variously given; the above formula corresponds with the result of my analysis. I obtained 73·60 mercury, 13·30 chlorine, 6·90 ammonia, and 6·20 water.

pure water, in an earthen dish (if hot water has been used, the solution must be allowed to cool perfectly), and caustic solution of ammonia added so long as a precipitate is caused. $1\frac{1}{2}$ Parts of ammoniacal solution, spec. grav. 0·960, effect this entirely. After standing 24 hours, the supernatant saline liquor is poured off, the precipitate thrown on a filter, without further washing, dried at a gentle heat, and kept in bottles not exposed to the light. The weight is that of the corrosive sublimate used.

(*b*) *With Carbonate of Soda.*—Several pharmacopœias direct this preparation to be precipitated with fixed alkaline carbonates. If this method is employed the process is as follows; 4 parts of perchloride of mercury, and 1 part of sal ammoniac are dissolved at the ordinary temperature in an earthen dish with 120 parts of pure water, a solution of carbonate of soda is to be added as long as it causes a precipitate, but any considerable excess must be carefully avoided. From $5\frac{1}{2}$ to 6 parts of crystallized carbonate of soda will be sufficient. The supernatant liquid is decanted, the precipitate allowed to subside, freed as much as possible from the adhering saline solution, by treating once or twice with pure water, thrown on a filter and dried with a gentle heat. The product nearly equals the weight of the perchloride of mercury employed.

Of course carbonate of potash may be used as well as carbonate of soda, but that obtained from potashes is objectionable as always containing silica, whilst it is too expensive when prepared from cream of tartar.

Recapitulation.—(*a*) When solution of ammonia is added to a solution of perchloride of mercury, the chlorine of one-half of the latter unites with ammonium, formed by 1 at. of ammonia NH_3, abstracting 1 at. of hydrogen from a second atom of ammonia to ammonium $= NH_4$; the liberated mercury unites

with the atom of NH_2, to which the name of amidogen has been given.

The chloride of ammonium formed, remains in solution, and the amide of mercury combines with the undecomposed perchloride of mercury to form the white precipitate.

2 at. HgCl, and 2 at. NH_3, form
1 at. NH_4Cl. and 1 at. $HgCl + NH_2Hg$.

3386 Parts of perchloride of mercury require 426 parts of anhydrous ammonia or 4260 parts of spec. grav. 0·960 (=10 per ct. of anhydrous). The solution must not be warm, otherwise the precipitate will be partially decomposed and yellow, from 1 at. of the precipitate with 2 at. of water forming sal ammoniac and peroxide of mercury, which combining with the second atom of the precipitate is the yellow substance :

2 at. $HgCl + NH_2Hg$, and 2 at. HO, form
1 at. NH_4Cl, and 1 at. $(HgCl + NH_2Hg) + 2HgO$.

Continued washing causes a similar decomposition and is hence to be avoided as much as possible ; the greater part of the sal ammoniac formed, remains in the solution, but if the precipitate is not washed it will also contain a small portion, the quantity is however extremely trifling and, as it does not in the least interfere with its properties, is very preferable to the chemical change the preparation undergoes from the action of water.

(*b*) The perchloride of mercury which alone is slightly soluble in water, is taken up in considerable quantities when sal ammoniac is present, owing to the formation of double salts ; of these two exist, the first, consisting of equal atoms of perchloride of mercury and sal ammoniac, has long been known under the name of Alembroth salt ; the other which consists of 2 atoms of perchloride of mercury combined with 1 at. of sal ammoniac is interesting in

the present case, as the salt from which the white precipitate is formed by alkaline carbonates.

When a solution of this double salt ($NH_4Cl + 2HgCl$) is mixed with a solution of carbonate of soda, the carbonic acid is liberated from 2 at. of the latter, the oxygen of the 2 at. of soda forms water with 2 at. of hydrogen of the ammonium, and the reduced sodium unites with the chlorine of the sal ammoniac and one atom of corrosive sublimate to form chloride of sodium; the mercury thus liberated combines with the amidogen NH_2, and this compound combined with the other atom of perchloride precipitates with 2 atoms of water.

1 at. NH_4Cl, 2 at. $HgCl$, and 2 at. $NaO + CO_2$, form
2 at. $NaCl$, 2 at. CO_2, and 1 at. $HgCl + NH_2Hg + 2HO$.

3386 Parts of perchloride of mercury and 668 parts of sal ammoniac require 3590 parts of crystallized carbonate of soda. The precipitate is a hydrate of the compound obtained by precipitation with ammonia. It may also be considered as a compound of 1 at. of chloride of ammonium and 2 at. of peroxide of mercury $= NH_4Cl + 2HgO$, but the above formula corresponds better with the other preparation. An excess of the precipitant must be avoided as much as possible, from its readily decomposing the white precipitate, and producing the same yellow body as is caused by continued washing or boiling, (*vide supra*) chloride of sodium and carbonate of ammonia being formed.

2 at. $HgCl + NH_2Hg + 2HO$, and 1 at. $NaO + CO_2$, form
1 at. $NaCl$, 1 at. $NH_4O + CO_2$, and 1 at. $(HgCl + NH_2Hg) + 2HgO$.

The carbonate of soda ordered,—viz. 6 parts to 4 of perchloride of mercury, — is in excess according to calculation, but is requisite on ac-

count of the formation of a portion of bicarbonate of soda; the carbonic acid liberated from 2 at. of carbonate of soda is not instantly given off, but remains partially dissolved in the supernatant liquid, and partly combined with another portion of the carbonate of soda. In order to prevent the bicarbonate of soda having a decomposing action on the precipitate, the quantity of sal ammoniac is increased, causing the formation of bicarbonate of ammonia and chloride of sodium, which are by no means detrimental.

In order to remove the common salt formed during the precipitation, it is necessary to treat it a few times with fresh water, although this not only causes a trifling decomposition, but also a loss. If, as in the precipitation by ammonia, it is not washed previous to drying, the salt will not answer one of its characteristic properties, viz. entire volatilization on heating, owing to the presence of the chloride of sodium.

Properties.—White precipitate prepared by either method forms when dry a snow-white mass, which is odourless, but possesses a nauseous metallic taste. That thrown down with ammonia entirely volatilizes when heated, *without fusing*, and forms ammonia, nitrogen, and calomel:—

3 at. $HgCl + NH_2Hg$, form
3 at. Hg_2Cl, 2 at. NH_3, and 1 at. N.

The other precipitate when heated *fuses* to a yellow liquid, and then volatilizes; the products of decomposition, excepting the water, are similar. Water takes up about $\frac{1}{600}$ part of white precipitate; hydrochloric and nitric acids dissolve it readily. Fixed alkalies and alkaline earths cause the evolution of half its ammonia and colour it yellow.

HYDRARGYRUM CYANATUM.

Hydrargyri Cyanidum.—Cyanide of Mercury.

FORMULA: $Hg + C_2N = HgCy$.

Preparation.—2 Parts of crystallized ferrocyanide of potassium are dissolved in 16 parts of water, the solution poured into a glass flask, and 3 parts of dry persulphate of mercury added, the whole boiled in a sand bath for half-an-hour, filtered, and with constant stirring, evaporated to dryness. The dry saline mass is finely powdered, digested with eight times its weight of alcohol of 80 per ct. for some hours, filtered whilst hot, the residue washed on the filter with hot alcohol, and the solution put in a cool place. After remaining quiet for some days, the crystals are separated from the mother liquor, the latter evaporated to dryness, the crystalline mass dried with a gentle heat and kept in a bottle excluded from the light. The product will be about 2 parts of salt.

Cyanide of mercury is generally made by digesting 2 parts of peroxide of mercury and 1 part of pure Prussian blue with 16 parts of water, filtering, and crystallizing. A basic salt is always formed in this process, which leaves even after crystallizing repeatedly a brown insoluble residue, and is never free from an alkaline reaction. When this method is followed, it is better after separating the magnetic oxide of iron, to supersaturate the solution with hydrocyanic acid (very little will be sufficient), filter, and then evaporate to crystallization. The produce will be rather more than 2 parts.

Recapitulation.—On bringing together ferrocyanide of potassium = $2KCy + FeCy + 3HO$, and persulphate of mercury = $HgO + SO_3$, the oxygen of the oxide of mercury forms with the potassium, potash;

this again combines with the sulphuric acid to neutral sulphate of potash; the mercury and cyanogen unite, and in combination with cyanide of iron form an insoluble precipitate. :—

1 at. $2KCy + FeCy + 3HO$, and 2 at $HgO + SO_3$, form
2 at. $KO + SO_3$, 1 at. $2HgCy + FeCy$, and 3 at. HO.

2642 Parts of crystallized ferrocyanide of potassium require 3700 parts of persulphate of mercury. The precipitate which forms, separates even at the ordinary temperature, and still more quickly by boiling, into soluble cyanide of mercury and insoluble protocyanide of iron: the latter is really a white precipitate, but owing to its great affinity for oxygen, attracts it from the air, becoming partly converted into Prussian blue (proto- and percyanide of iron) and (hydrated) oxide of iron; being according to the extent of its change of green or bluish colour :—

9 at. FeCy, and 3 at. O, form
1 at. $3FeCy + 2Fe_2Cy_3$, and 1 at. Fe_2O_3.

To separate the cyanide of mercury, still in solution, from the sulphate of potash, the filtrate must be evaporated to dryness and exhausted with alcohol, which leaves the sulphate of potash undissolved.

On digesting Prussian blue with peroxide of mercury and water, the cyanogen combines with the mercury, and the iron forms, with the oxygen, blackish-brown flakes :—

1 at. $3FeCy + 2Fe_2Cy_3 + 9HO$, and 9 at. HgO, form
9 at. HgCy, 3 at. $FeO + HO$, and 2 at. $Fe_2O_3 + 3HO$.

6388 Parts of pure Prussian blue require 12150 parts of peroxide of mercury. It is a peculiarity

in this process, that although with the above proportions, some of the Prussian blue remains unaltered, yet all the oxide of mercury is decomposed, and a basic cyanide of mercury is formed. With a large excess of oxide of mercury, the Prussian blue is entirely decomposed; but, at the same time, this does not prevent the formation of the basic salt. The basic salt is readily soluble in water, the solution having a strongly alkaline reaction, and yielding, on evaporation, besides a reddish precipitate which consists of oxide of mercury and a trace of cyanide of mercury, crystalline needles, that on resolution and evaporation yield the same appearances. It is therefore the better plan to neutralize the clear solution with prussic acid, which causes the precipitation, as proto-cyanide of iron, of a small portion of protoxide of iron still in solution, again to filter, and then crystallize.

Properties.—Cyanide of mercury crystallizes in white, more or less transparent, four-sided prisms and pyramids, which are odourless, but have a pungent nauseous metallic taste. Heated in a closed glass tube the crystals fly in pieces, fuse, and decompose into cyanogen and mercury; the separation of the former from the latter is, however, not perfect, a portion forming an isomeric variety, PARACYANOGEN, which remains as a black carbonaceous mass. The salt dissolves in water and alcohol; the former, at the ordinary temperature, takes up $\frac{1}{11}$, at the boiling $\frac{2}{3}$ of its weight; alcohol, of 80 per ct., $\frac{1}{20}$ its weight, at the ordinary temperature, and $\frac{1}{3}$ when boiling. These solutions have no action on either litmus or turmeric paper.

HYDRARGYRUM IODATUM.

Hydrargyri Iodidum.—Proto-Iodide of Mercury.

FORMULA: Hg_2I.

Preparation.—8 Parts of mercury are triturated, in a porcelain mortar, with a few drops of alcohol and 5 parts of iodine, until the whole is converted into a dark yellowish-green powder, and even under the magnifying glass exhibits no trace of metallic globules. During the operation, the mortar should be covered with a cloth, to prevent the action of the light. Sufficient alcohol is then added, constantly triturating, to convert it into a thin paste, this is thrown on a filter, and, excluding the light, washed with alcohol until on passing off the latter no longer gives a black precipitate or turbidness with sulphuret of ammonium, the contents of the filter dried with a very gentle heat, and kept in a bottle away from the light. The weight of product should equal that of the mercury and iodine employed.

Recapitulation.—On rubbing together mercury and iodine, they acquire at first a red colour, from the formation of periodide, which, as the mercury enters more and more into combination, becomes green, and finally, when the above proportion of ingredients has been employed, of a dark yellowish green:—

2 at. Hg, and 1 at. I, form
1 at. Hg_2I.

2500 Parts of mercury require 1586 parts of iodine. The small quantity of alcohol so far facilitates the combination, that it gradually dissolves all the iodine. The application of heat is unnecessary, and even a disadvantage, as causing the iodine to evaporate. By washing the prepara-

tion, a small trace of periodide of mercury will be removed.

Properties.—Proto-iodide of mercury is a dark greenish-yellow odourless and tasteless powder; heated in a test tube it becomes at first reddish, separating into periodide and metallic mercury, then yellowish, fusing to a brown liquid, and finally volatilizing; the iodine passing off first, and then the metal. In the light it decomposes, acquiring a gray appearance. It is insoluble in water and alcohol. Boiling hydrochloric acid dissolves it, but only slowly, the solution containing perchloride and periodide:—

1 at. Hg_2I, and 1 at. ClH, form
1 at. HgI, 1 at. HgCl, and 1 at. H.

Proto-iodide is quickly reddened by nitric acid, half of the mercury being abstracted and forming per-nitrate; on cooling, a portion of the per-iodide formed separates as glittering scarlet scales:—

3 at. Hg_2I, and 4 at. NO_5, form
3 at. HgI, 3 at. $HgO + NO_5$, and 1 at. NO_2.

Iodide of potassium decomposes the proto-iodide of mercury into periodide, which dissolves, and metallic mercury. Should the preparation be of a yellow colour, it contains some quantity of *per-iodide*, and this is generally the case when prepared by the moist way. Small quantities of periodide are detected by agitating with alcohol, which dissolves it, filtering and evaporating, when the residue formed is red.

HYDRARGYRUM BINIODATUM.

Hydrargyri Periodidum.—Periodide of Mercury.

Formula: HgI.

Preparation.—Periodide of mercury is obtained most pure and beautiful by the moist way. 5 Parts

of perchloride of mercury are dissolved in 100 parts of water, and a solution of iodide of potassium, dissolved in 10 times its weight of water, added so long as a precipitate forms, taking care that the precipitant is not in excess. From 6—7 parts of the latter will be necessary, according to its state of purity. The precipitate is allowed to subside in a dark place, washed by repeated decantation, collected on a filter, dried with a very gentle heat, and kept, free from access of light, in a closed bottle. The produce will be 8 parts.

Recapitulation. — Perchloride of mercury and iodide of potassium mixed in the proper proportions exchange their elements, and form readily-soluble chloride of potassium, and insoluble periodide of mercury :—

1 at. $HgCl$, and 1 at. KI, form
1 at. KCl, and 1 at. HgI.

1693 Parts of perchloride of mercury require 2076 parts of iodide of potassium. At first, whilst the mercury is in excess, a yellow precipitate is formed, which is a compound of equal atoms of perchloride and periodide of mercury; but on the addition of more iodide of potassium, this perchloride is converted into periodide, and the yellow colour changed to scarlet. By excess of the precipitant, the periodide of mercury is readily dissolved, and in consequence is lost on washing. If the iodide of potassium contains chloride, as is generally the case, it is only necessary to use rather more than is required theoretically, other than this it is not detrimental.

Properties.—Periodide of mercury, thus prepared, forms a brilliant scarlet powder, odourless, and without taste. Heated in a test tube it becomes yellow, fuses to a brownish-yellow liquid, and sublimes to a yellow crystalline mass, which acquires a red colour partially on cooling, and entirely, either more or less gradually. Water dis-

solves only a trace of it. Alcohol, of 80 per ct., $\frac{1}{120}$ of the salt in the cold, and $\frac{1}{12}$ at the boiling point. The hot saturated solution deposits yellow scales on cooling, which gradually become red. It dissolves also in hydrochloric and nitric acids, especially on heating, with the evolution of hydriodic acid and free iodine; the solution contains, according to the duration of the action, besides the iodide, variable quantities of perchloride and pernitrate; and, on cooling, deposits a portion of the per-iodide in a crystalline state. Iodide of potassium dissolves it with the greatest readiness, and thus quickly separates it from *minium*, *cinnabar*, or substances having a similar appearance.

HYDRARGYRUM OXIDATUM RUBRUM.

Hydrargyri Peroxidum.—Peroxide of Mercury.—Red Precipitate.

FORMULA: HgO.

Preparation.—1 Part of mercury is digested, in a glass bottle, on a sand bath, with 3 parts of nitric acid, spec. grav. 1·20, until all the mercury has disappeared. The solution is poured into a porcelain dish, and evaporated, with continued stirring over an open fire, to dryness. The dried yellowish-white mass is intimately mixed with as much mercury as has been dissolved, then returned to the dish, and, with continuous stirring, it is heated over an open fire, at first gently and then rather strongly, until no more brownish-yellow fumes are evolved, and the powder has a grayish-black appearance. The dish is now removed from the fire, its contents mixed with crystallized carbonate of soda, $\frac{1}{10}$ the weight of the mercury employed, the whole boiled for half an hour with a measured quantity of water, thrown on a filter, and washed with warm water

until all the alkali is removed, dried with a gentle heat and kept in a vessel excluded from the light. The product is rather more than the weight of the mercury employed.

Recapitulation.—The mercury is very readily acted on by nitric acid, brownish-yellow vapours being given off; at first when the acid is in excess, protoxide is formed, but on exposing the solution to heat and evaporating, all the protoxide is gradually converted into peroxide, and the process is explained as follows:—

3 at. Hg, and 4 at. NO_5, form
3 at. $HgO + NO_5$, and 1 at. NO_2.

3750 Parts of mercury require 2700 parts of anhydrous nitric acid, or 10,000 parts of hydrated, of spec. grav. 1·20 = 27 per ct. of anhydrous. The fourth atom of acid serves for the oxidation of the metal, causing the formation of nitric oxide which in contact with the air forms hyponitric acid. In the proportions of 1 part of metal and 3 of acid there is an excess of the latter, which is requisite to supply the waste which occurs from evaporation during the solution of the metal. By evaporation to dryness, the neutral compound gives off half its acid, and remains as a basic per-nitrate of mercury = $2HgO + NO_5$, in which there is still present, as nitric acid, more oxygen than is required to oxidize an equivalent portion of metal; for

1 at. $2HgO + NO_5$, and 2 at. Hg, form
4 at. HgO, and 1 at. NO_5.

And on this account, in order to economise the acid, as much mercury is added to the salt as it already contains. The nitrous acid, which on heating is liberated, attracting oxygen from the air, appears as brown-yellow vapours. The heat must at first be applied very gently, otherwise a portion of the metallic mercury will be given off as such, and thus

cause a loss of product. The mass at first yellow, will gradually become darker, and finally almost black; on cooling it assumes a brick-red colour, but some few yellow grains of a basic salt $= 4HgO + NO_5$ are generally perceptible. The last traces of nitric acid are driven off with difficulty, and at the risk of reducing a portion of the oxide; consequently it is better when the powder has been heated to the point above mentioned, to allow it to cool, and remove any traces of acid present, which will be but inconsiderable, by boiling with a weak solution of soda.

Properties.—Oxide of mercury thus prepared, forms a brick-red crystalline powder, odourless, but of a faintly nauseous metallic taste. Heated it acquires nearly a black colour, which on cooling again becomes red. More strongly heated it separates into oxygen and metal. Water dissolves traces of it: alcohol none: nitric and hydrochloric acids on the other hand dissolve it readily. Any contamination with nitric acid (as the basic salt) may be generally detected from the appearance of yellow grains, but is determined with certainty by boiling with a solution of soda, filtering, supersaturating the filtrate with sulphuric acid and adding a drop of solution of indigo, the blue colour of which, if nitric acid is present, will be destroyed on warming. The soda abstracts the acid from the basic salt, it is again liberated by sulphuric acid, exerting in its free state a destructive action on indigo. The preparation is also adulterated in the shops. *Cinnabar* is scarcely to be expected from its high price: should it be present, sulphurous acid will be given off on heating the preparation with charcoal; heated in contact with the latter, the cinnabar separates into metal and sulphur, the last body being converted by the oxygen of the air into sulphurous acid. Besides this, the best test of its purity is to heat a portion of the oxide in a small retort or porcelain crucible, when no residue (as

oxide of lead, brick dust, &c.) must occur. Red oxide of lead is known by the dark-brown residue of peroxide of lead (PbO_2,) which remains on agitating with dilute nitric acid. The red lead, or minium, consists of Pb_3O_4, and is converted by nitric acid into soluble oxide and insoluble peroxide.

1 at. Pb_3O_4, and 2 at. NO_5, form
2 at. $PbO + NO_5$, and 1 at. PbO_2.

Brick dust being only partially dissolved by nitric acid will form a red residue, which will also contain iron. On heating a portion of oxide in which all three contaminations are present, on charcoal before the blowpipe, the oxide and cinnabar will volatilize with the evolution of sulphurous acid fumes, the minium will be reduced to metallic globules, whilst the brick dust will remain unaltered on the charcoal.

HYDRARGYRUM OXIDATUM SULPHURICUM.

Hydrargyri Sulphas.—Neutral Persulphate of Mercury.

FORMULA: $HgO + SO_3$.

Preparation.—6 Parts of mercury, $3\frac{1}{2}$ parts of concentrated sulphuric acid, 3 parts of water, and 4 parts of nitric acid, spec. grav. 1·20, are digested in a flask, on a sand bath, so long as brownish-yellow vapours are evolved; the flask is emptied into a porcelain dish, the latter placed over an open fire, not too strong, and evaporated with constant stirring to dryness, or until fumes are no longer evolved. The dry white saline mass is kept in a closed vessel away from the light. It will produce nearly 9 parts.

Recapitulation. — Compare it with the article CUPR. OXID. SULPH. In the same manner,

3 at. Hg, 3 at. SO_3, and 1 at. NO_5, form
3 at. $HgO + SO_3$, and 1 at. NO_5.

3750 Parts of mercury require 1839 parts of hydrated sulphuric acid, and 2500 parts of nitric acid spec. grav. 1·20. By evaporating to dryness the water and slight excess of sulphuric acid are removed.

In regard to the method ordinarily employed of preparing it without nitric acid, I must also refer to the article CUPR. OXID. SULPH.

Properties.—The neutral persulphate of mercury is a white crystalline powder, odourless but of a pungent saline nauseous metallic taste. Heated it becomes yellow, then brown, but again assumes its white colour on cooling; strongly heated, it fuses to a brown liquid and volatilizes completely, forming a white crystalline sublimate. In this last process a portion of the salt will be reduced to sulphuric acid and oxide, the latter again into metal and oxygen; and, consequently the sublimate from the presence of the free metal will exhibit in some places a greyish appearance. Water separates the salt into a basic one, which subsides, and an acid one which is soluble:

4 at. $HgO + SO_3$, form
1 at. $3HgO + SO_3$, and 1 at. $HgO + 3SO_3$.

This basic salt $= 3HgO + SO_3$, the so called Turpeth mineral (Hydrargyrum subsulphuricum), which is also prepared by boiling the neutral salt with water, washing and drying the residue, is a lemon-yellow tasteless powder, partially soluble in water. Heated it separates into neutral salt and oxide, and volatilizes completely; the sublimate, owing to its admixture with metal, has a grey instead of a white appearance.

HYDRARGYRUM PROTOXIDATUM PURUM.

Hydrargyri Protoxidum.—Hydrargyri Oxidum Cinereum.—Pure Protoxide of Mercury.—Black Oxide of Mercury.

FORMULA: Hg_2O.

Preparation.—1 Part of finely divided calomel, that prepared by precipitation is to be preferred, is treated in a porcelain mortar with 1 part of caustic potash solution, spec. grav. 1·333, which has previously been diluted with 3 parts of water; after rubbing together for about half-an-hour it is thrown on a filter, the residue protected as much as possible from the light and washed with cold water as long as the fluid passing from it exhibits an alkaline reaction, dried at the ordinary temperature, and kept in a vessel excluded from light. 1 Part of calomel yields $\frac{9}{10}$ of protoxide.

Recapitulation.—The elements of the proto-chloride of mercury and caustic potash are exchanged, forming protoxide of mercury and chloride of potassium.

1 at. Hg_2Cl, and 1 at. KO, form
1 at. Hg_2O, and 1 at. KCl.

2943 Parts of calomel require 590 parts of potash, or 2269 parts of potash solution, spec. grav. 1·333 (= 26 per ct. of pure potash); an excess of the latter is however necessary to insure the entire decomposition of the calomel, of which the precipitated, as being more finely divided, is to be preferred. Heat during the process is carefully to be avoided, as causing the protoxide to separate into peroxide and metal. Nevertheless with every precaution, a small portion will decompose, and during the washing and drying the black colour becomes tinged with green.

Properties.—Pure protoxide of mercury should really be quite black, but from the presence of a

little peroxide, it has generally a green tinge. It is odourless and tastelesss, insoluble in water and alcohol. Heated it acquires at first a red colour, from decomposition into oxide and metal, it then becomes darker, separating into oxygen and metal, and volatilizes without leaving a residue. If on agitating it in water, the latter gives with nitrate of silver a white precipitate *chloride of potassium* is present. Dilute nitric acid readily dissolves it. Rubbed with dilute hydrochloric acid it becomes converted into a grey powder (a mixture of calomel and metal,) whilst any oxide present remains in solution and yields with caustic potash a yellow precipitate.

HYDRARGYRUM PROTOXIDATUM ACETICUM.

Hydrargyri Acetas.—Proto-Acetate of Mercury.

FORMULA: $Hg_2O + \bar{A}$.

Preparation.—8 Parts of crystallized proto-nitrate of mercury are intimately rubbed up in a porcelain mortar with 16 parts of water and 1 part of nitric acid, spec. grav. 1·20; the whole thrown into a glass flask, 60 parts of water added, and digested with a gentle heat until the salt is dissolved, then filtered, the solution diluted with twice its weight of water, and precipitated with a solution of acetate of potash; of the latter 5—6 parts will be necessary. The precipitate is excluded from the light, allowed to subside, collected on a filter, washed with a little water, dried without artificial heat, and kept in a closed vessel with the previously-mentioned precaution. The yield should be $7\frac{1}{2}$ parts.

Recapitulation.—Neutral proto-nitrate of mercury requires for its complete solution in water the addition of a little free nitric acid; (*Vide* HYDRARG.

Protox. Nitr.). Acetate of potash causes in this solution a bulky precipitate of difficultly-soluble acetate of protoxide of mercury, as white scales; the whole of the nitrate of potash remaining in the solution:

1 at. $Hg_2O + NO_5 + 2HO$, and 1 at. $KO + A$, form 1 at. $Hg_2O + \bar{A}$, 1 at. $KO + NO_5$, and 2 at. HO.

For 3500 parts of the salt of mercury only 1228 parts of acetate of potash would be requisite; but from the presence of the free nitric acid more is necessary, whilst acetic acid is liberated. If the solution were not considerably diluted, the bulky precipitate would not subside properly, and thus necessitate a continued washing on the filter.

Properties.—Proto-acetate of mercury forms fine silvery scales, which have a soft unctuous feel, a faint odour of acetic acid, and a feebly metallic taste; heated in a glass tube it fuses, gives off acetic acid, blackens, whilst a portion of the acid forms with the oxygen of the salt several products (as carburetted hydrogen, carbonic acid, acetone), leaving behind carbon and metallic mercury, which last is finally volatilized. If the heating is performed in the open air the carbon also is consumed, leaving no residue. In water it dissolves with difficulty, 1 part of salt requiring more than 300 parts of cold, but far less warm water; the solution has an acid reaction, and if boiled, separates into a persalt, which remains dissolved, and metal, which subsides as a gray powder. Cold alcohol has no action on it, but boiling alcohol converts it into soluble persalt and metal. If the precipitate has not been thoroughly washed, it leaves on heating in the air a residue of carbonate of potash; the nitrate of potash present giving up its oxygen to the carbon, nitric oxide and carbonic acid are evolved, a portion of the latter combining with the potash.

HYDRARGYRUM PROTOXIDATUM NITRICUM.

Hydrargyri Nitras.—Proto-Nitrate of Mercury.

FORMULA: $Hg_2O + NO_5 + 2HO$.

Preparation.—1 Part of mercury and 2 of nitric acid, spec. grav. 1·17 are weighed into a flat-bottomed flask, the mouth of which is covered with a watch glass, and digested with constant agitation, without heat, until no more yellowish-brown vapours are perceptible, and the metal is almost entirely converted into a white saline mass. In the summer the flask must be kept in the cellar during the digestion, or cooled with water. According to the quantity of material, the digestion will require from 4 to 20 days. The saline mass is collected on a funnel, the bottom of which is loosely stopped with a glass stopper, washed with about half as much cold water as the acid liquid which escaped, spread on a flat dish, dried on slightly warm sand, and kept in a closed bottle, excluded from the light. The yield is about equal to the mercury employed.

Recapitulation.—Mercury, in contact with dilute nitric acid, is, in the cold, almost entirely converted into protoxide, which, combining with another portion of acid and water, forms a difficultly-soluble salt. The yellowish-brown vapours that separate are hyponitric acid, $=NO_4$, formed by the action of the air on nitric oxide:—

6 at. Hg, 4 at. NO_5, and 6 at. HO, form
3 at. $Hg_2O + NO_5 + 2HO$, and 1 at. NO_2.

7500 Parts of mercury should require only 2700 parts of anhydrous nitric acid, or 11250 parts of hydrated, of spec. grav. 1·17, which contains 27 per ct. of anhydrous acid. In order to obtain the neutral salt, a large excess of acid is necessary,

otherwise a basic salt, $=3Hg_2O+2NO_5+3HO$, is formed, even in the cold. In spite of the large excess of acid, a small portion of metal, (about $\frac{1}{10}$) remains unacted on, which is unavoidable and of but slight consequence, as, the salt being almost always used in solution, the excess of metal is separable by filtration.

By warming the flask when the cold digestion is finished, the separation of the mercury and salt is effected, the latter being entirely dissolved; the process, however, has this disadvantage, the crystals do not again separate on cooling, but require a further evaporation, and, instead of the firm compact crystalline mass, they are deposited as a pasty magma of fine crystalline needles, which are not free from some portions of the yellow basic salt, $=2Hg_2O+NO_5+HO$; consequently, it is better to preserve the salt for use in the state in which it is obtained by cold digestions. The saline mass, in this case, often exhibits, during the digestion, traces of yellow colour, from the formation of a basic salt; by agitation with the acid solution, this is again dissipated. The reason why the salt obtained does not exceed the quantity of metal used, is, that $\frac{5}{7}$ of the latter only will be found in the salt, and $\frac{2}{7}$ in solution; from motives already explained, it is not advisable to employ this to form a persalt, but rather to evaporate it with the wash water to dryness, and re-obtain the mercury as red oxide; (*Vide* HYDRARG. OXID. RUB.).

Properties.—Proto-nitrate of mercury, thus prepared, exists as groups of white, heavy, transparent, four or six-sided prisms, between some of which globules of mercury are enclosed. It reddens litmus paper powerfully, has a feeble smell of nitric acid, and a sharp, bitter, metallic taste. Exposed to the sunlight for some time, its external appearance is not changed, being, as regards light, the most stable of all mercurial salts. Heated it fuses,

evolving aqueous vapours, and the yellowish-brown vapours of hyponitric acid, leaving peroxide of mercury, which is finally decomposed into metal and oxygen, and volatilizes without a residue. Water containing nitric acid, spec. grav. 1·20, about $\frac{1}{8}$ of the weight of the nitrate of mercury, dissolves this salt entirely, leaving only the uncombined metallic mercury. Pure water exerts a decomposing action on the salt, converting it, as was generally supposed, into a basic and acid salt, but Rose has shown, that it rather becomes a persalt and free metal. For instance, on boiling the salt with water, it becomes of a dirty-yellow colour, the oxide of a portion of the salt forms metal and peroxide, which, retaining a part of the acid, forms the Salpetre-Turpeth $= 4HgO + NO_5$, whilst the liberated acid combines with a portion of the still-undecomposed protosalt, (as well as with traces of peroxide). The dirty-yellow substance is a mixture of metal, basic persalt, and undecomposed proto-salt; whilst in the solution are acid proto-nitrate, and traces of oxide. If the acid solution is decanted, and the yellow body again treated with water, it finally becomes gray, owing to the remaining portion of proto-salt undergoing the same decomposition, and the basic persalt losing all its acid; the residue is metallic mercury and peroxide of mercury. Cold water has a more tardy, but similar action to boiling.

HYDRARGYRUM PROTOXIDATUM NITRICUM AMMONIATUM.

Hydrargyri Ammonio-Nitras.—Ammoniated Proto-Nitrate of Mercury.—Hahnemann's Soluble Quicksilver.

FORMULA :

$$(Hg_2O + NO_5) + NH_2Hg_2 + xHg + x(HgO + NO_5) + NH_2Hg.$$

Preparation.—8 Parts of dry proto-nitrate of mercury are triturated, in a porcelain mortar, with 16 parts of pure water, in which is mixed 1 part of nitric acid, spec. grav. 1·20; to this is added about 60 parts of pure water, and the whole gently warmed until dissolved, filtered if necessary, the clear solution diluted with eight times its weight of water, and, with continuous stirring, a mixture of $3\frac{1}{2}$ parts caustic ammonia, spec. grav. ·960, and 10 parts of water, added to it. After the black precipitate thus formed has subsided the supernatant liquid is decanted, the same quantity of water is again added and decanted, the whole then thrown on a filter, and washed so long as the fluid passing off has an acid reaction, dried with a gentle heat, and kept in vessels excluded from light. Its weight should equal $3\frac{1}{2}$ parts.

Recapitulation.—When a solution of proto-nitrate of mercury comes in contact with caustic ammonia, as in the process just described, half of the mercurial salt will be decomposed; the acid combines with half the ammonia, which, by abstracting 1 at. of hydrogen from the other atom of ammonia, and the oxygen from the protoxide of mercury—(that is to say, by the absorption of the elements of 1 at. of water)—has become converted into oxide of ammonium, to soluble nitrate of oxide of ammonium. The portion of ammonia deprived of 1 at.

of its hydrogen, or amidogen, $=NH_2$, combining with the deoxidized mercury, forms amide of mercury, $=NH_2Hg_2$, and finally combines with the other half of the proto-nitrate of mercury to a black precipitate :—

2 at. $Hg_2O + NO_5$, and 2 at. NH_3, form
1 at. $NH_4O + NO_5$, and 1 at. $(Hg_2O + NO_5) + NH_2Hg_2$.

7000 Parts of crystallized proto-nitrate of mercury should require, from the above proportions, 426 parts of anhydrous ammonia, or 4260 of hydrated, =10 per ct. This quantity of ammonia is, however, on no account to be used, but the supernatant liquor must retain a perceptibly acid reaction, otherwise the nitrate of ammonia formed exerts a decomposing action on the black precipitate, changing it gray. Nitrate of ammonia shows a great disposition to form a readily-soluble double salt with pernitrate of mercury, and to accomplish this it first reduces the black precipitate into metallic mercury and a compound of nitrate of amide of mercury, which has a white appearance :—

1 at. $(Hg_2O + NO_5) + NH_2Hg_2$, form
2 at. Hg, and 1 at. $(HgO + NO_5)NH_2Hg$.

The nitrate of ammonia and the white compound are then converted into ammonia, which is evolved, and into pernitrate of mercury :—

1 at. $(HgO + NO_5) + NH_2Hg$, and 1 at. $NH_4O + NO_5$, form
2 at. NH_3, and 2 at. $HgO + NO_5$;

and finally the pernitrate of mercury, combining with 2 other atoms of nitrate of ammonia, forms the readily-soluble double salt. This decomposition of the black substance proceeds most quickly when it is treated with a concentrated solution of nitrate of ammonia ; the precipitate is then dis-

solved, especially on warming, with a strong evolution of ammonia, and a trifling gray residue of metallic mercury.

The solutions are directed to be very dilute, as in this case the action is not so energetic. Nevertheless, the entire decomposition of the black precipitate is not to be prevented, as with every drop of ammonia a portion of nitrate of ammonia is formed; besides its chief constituents, there are also found in the precipitate, protonitrate of amide of mercury $= (Hg_2O + NO_5 + NH_2Hg_2)$, metallic mercury, and pernitrate of amide of mercury $= (HgO + NO_5 + NH_2Hg)$, even when it has a black appearance, but the proportion of metallic mercury is larger than that of the white body, as the latter is dissolved by the nitrate of ammonia. In consequence of this, the decomposition, or increase of the white body, is in proportion to the ammonia used, and if this be largely in excess, a gray instead of a black precipitate is the result, therefore ammonia must be added only so long as a black precipitate is formed; this point is attained when to 8 parts of protonitrate of mercury not more than $3\frac{1}{2}$ parts of Liq. Ammoniæ, spec. grav. ·960, are employed.

As may be seen from the yield, at least half the metal contained in the protonitrate will be found in the wash water; to regain it, solution of caustic potash is added, and the collected precipitate, when treated with nitric acid and heated, forms peroxide. (*Vide* HYDR. OXID. RUBR.)

Properties.—Hahnemann's mercurial precipitate is a velvety, black, odourless and tasteless powder, in which, when strongly magnified, globules of metallic mercury are perceptible. Heated in a closed glass tube, it becomes, without fusing, at first yellow, then reddish-brown, and finally volatilizes completely; the products which separate are water, metallic mercury, and nitric oxide:—

1 at. $(Hg_2O + NO_5) + NH_2Hg_2$, forms
2 at. HO, 2 at. NO_2, and 4 at. Hg.

The sublimate should really be of a gray colour, but the nitric oxide forms with the oxygen of the air hyponitric acid, which occasions a tolerably complete oxidation of the mercury, and, in consequence, forms a brown or reddish-yellow deposit in the tube, and a piece of litmus paper placed in the latter becomes strongly reddened. In water and alcohol the preparation is insoluble. In about 20 parts of concentrated acetic acid it is entirely soluble, excepting of course the metallic mercury, (often more than 20 per ct.); in the cold the solution deposits lustrous silvery scales of proto-acetate of mercury. Nitric acid, spec. grav. 1·20 dissolves it, leaving at first the white precipitate, which by continued action in the heat finally disappears. Caustic potash evolves ammonia from it. If the preparation has a gray appearance, too much ammonia has been employed in its precipitation, and it contains an excess of the white compound. If adulterated with black *sulphuret of silver*, the smell of sulphurous acid is perceptible when heated on charcoal.

HYDRARGYRUM PROTOXIDUM PHOSPHORICUM.

Hydrargyri Phosphas.—Protophosphate of Mercury.

FORMULA: $2Hg_2O + P_2O_5$.

Preparation.—A dilute solution of 8 parts of protonitrate of mercury, prepared as in the foregoing article, is treated with a solution of crystallized phosphate of soda so long as a precipitate is formed, (about 5 parts are necessary) the latter carefully washed with water, as long as this acquires

an acid reaction, dried with a gentle heat, and kept in a bottle excluded from the light. Nearly 7 parts are the product.

Recapitulation. — Protonitrate of mercury and phosphate of soda exchange elements, protophosphate of mercury precipitating, and nitrate of soda remaining in solution :—

2 at. $Hg_2O + NO_5 + 2HO$ and 1 at. $(2NaO + HO + P_2O_5) + 24Aq.$ form
1 at. $2Hg_2O + P_2O_5$, 2 at. $NaO + NO_5$, and 27 at. HO.

7000 Parts of protonitrate of mercury require 4492 parts of crystallized phosphate of soda. On account of the excess of nitric acid requisite for the entire solution of the mercurial salt in water, the supernatant liquid has an acid reaction.

Properties.—Protophosphate of mercury is a white, fine, crystalline, odourless and tasteless powder. Heated, it fuses, evolving oxygen and metallic mercury, and leaving a colourless glacial mass, which is the phosphoric acid with a trifling quantity of mercury. In water it is insoluble, whilst nitric acid dissolves it on heating completely.

HYDRARGYRUM SULPHURATUM NIGRUM.

Hydrargyri Sulphidum.—Black Sulphuret of Mercury. —Æthiops Mineral.

FORMULA : $HgS + xS$.

Preparation.—Equal parts of mercury and washed flowers of sulphur are rubbed in a porcelain mortar, with the occasional addition of a few drops of water, until they form a grayish-black powder, and neither mercury nor sulphur is visible with a magnifying

glass; the labour is greatly diminished by employing diluted sulphide of ammonium instead of water.

In order to facilitate the combination, some pharmacopœias recommend the powder to be warmed during the trituration; whilst in others they are ordered to be fused. As the chemical constitution is modified by these different processes that of one's own pharmacopœia should be followed.

Recapitulation.—On rubbing together mercury and sulphur, a partial combination ensues even at the ordinary temperature; this is assisted by a few drops of water, and still more so by hydrosulphate of ammonia, which by dissolving the sulphur presents it in a soluble form to the mercury. In the proportions previously given, the sulphur is in considerable excess, even for the formation of the highest sulphuret HgS, consisting of equal atoms, or of 1250 parts mercury, and 200 sulphur; consequently the 1050 parts of sulphur must be considered an admixture, and even of the 200 parts a portion at least, instead of the highest sulphuret, forms the lowest sulphuret Hg_2S, or in other words, the 1250 parts of mercury hold less than 200 parts of sulphur in combination. If, when with an ordinary magnifying glass no more mercurial globules are visible, the preparation is examined under a microscope, the mass appears to consist principally of grayish-black globules, in which lie single glittering particles of metallic mercury. The colour of the gray-black globules is due to the chemical combination of sulphur and mercury HgS or Hg_2S: this compound is only superficial, the interior of the globules consisting of free sulphur. The yellow globules of sulphur become coated with a crust of sulphuret of mercury, and thus being enclosed, the free mercury present, in spite of the trituration, either remains as such or converts the HgS into Hg_2S. If the temperature is raised, less uncombined mercury will remain, as the sulphur is partially vola-

tilized and more readily comes in contact with the metal. Even when the preparation is fused it contains free sulphur, the colour of which is concealed by sulphuret of mercury.

Properties.—Æthiops mineral is a heavy, somewhat grayish-black, odourless and tasteless powder: soluble neither in water, hydrochloric nor dilute nitric acid; the latter taking up at the most only small traces of uncombined mercury. Heated in a test tube, it first loses sulphur, which deposits on the cool portion of the tube, and partly combines with the oxygen of the air present, to sulphurous acid; then sulphuret of mercury sublimes, and deposits itself as an iron-gray mass, becoming red when rubbed; if there is a residue, either the mercury or sulphur was impure. With a magnifying glass of moderate power no mercurial globules should be perceptible.

By mixing with equal parts of finely prepared sulphuret of antimony (Antimonium crudum), the Hydrargyrum stibiato sulphuratum (Æthiops antimonialis) is obtained.

HYDRARGYRUM SULPHURATUM RUBRUM.

Hydrargyri Persulphidum.—Red Sulphuret of Mercury.—Cinnabar.

Formula: HgS.

Preparation.—12 Parts solution of caustic potash, spec. grav. 1·333 are brought to the boiling point in a cast iron vessel, and whilst constantly stirring powdered sulphur is added as long as it is dissolved (about 4½ parts will be sufficient); the dark yellow solution is decanted from the excess of sulphur, sufficient water added to replace that evaporated, and filtered if necessary. When entirely cooled it is poured

into a thoroughly strong bottle, which must be only $\frac{4}{5}$ filled, and 8 parts of mercury added, the bottle well closed with a cork and bladder, and shaken continually until the whole of the metal is converted into a bright red powder. The length of time naturally depends on the quantity of materials employed. As the arm would soon become tired by the operation, it is advisable to employ some mechanical power, as a saw mill, &c., to keep the bottle in constant and powerful motion; in this case the bottle should previously be well packed with saw dust in a box to prevent its breaking. It is advisable not to put more than $1\frac{1}{2}$ or 2 pounds of solution into one bottle, and where a large quantity is being operated on to employ several bottles; the shaking should continue at least 24 hours. When the mercury is transformed into a bright red colour it is put into a dark place, the supernatant yellow liquid poured off as much as possible, the powder repeatedly washed, by decantation, with pure water so long as the latter acquires an alkaline reaction, separated from the heavy gray particles with which it is always mixed, by allowing them to subside first, the remainder collected on a filter and dried with a gentle heat. The yield of pure cinnabar will about equal in weight the mercury employed.

In most works the agitation is directed to be accompanied by heat, but in this case I have always obtained a preparation of a very inferior colour.

Recapitulation.—On boiling solution of caustic potash with excess of sulphur, 2 at. of potash give up their oxygen to 2 at. of sulphur, and form 2 at. of hyposulphurous acid = 2SO, which combine with potash to hyposulphite potash = KO + 2SO. The 2 at. of potassium, or potash deprived of its oxygen, take up 10 at. of sulphur, forming 2 at. of the highest sulphuret of potassium = KS_5 :—

3 at. KO and 12 at. S, form
1 at. KO + 2SO, and 2 at. KS_5.

1770 Parts of anhydrous potash or 6730 parts of solution spec. grav. 1·333 (=26·3 per. ct. of potash) require 2400 parts of sulphur; a slight excess of the latter is necessary, to indicate that the sulphur will take up no more. Experience teaches us that the highest sulphuret of potassium, by giving off 2 at. of sulphur and becoming reduced to a tersulphuret of potassium KS_3, is capable of converting nearly 2 at. of mercury into cinnabar. 2 At. of the highest sulphuret of potassium are sufficient for nearly 4 at. of mercury or 5000 parts; or, 12 parts of caustic potash solution spec. grav. 1·333 (when after boiling with excess of sulphur it is converted into the highest sulphuret) require 8 parts of metal. At the commencement of the agitation a black sulphuret of mercury is formed, (without doubt the lowest = Hg_2S, which by taking up more sulphur becomes HgS), gradually, however, acquiring the peculiar red colour of finely prepared cinnabar. This change of colour of the sulphuret of mercury from black to red, has been attributed to its passing from the amorphous to the crystalline state, from the fact that cinnabar prepared by the dry way previously to its sublimation, when it is undoubtedly amorphous, acquires during that process a crystalline and red appearance. For my own part, I consider that the change from the amorphous to the crystalline state, is rather due to the heat necessary for its sublimation, as cinnabar prepared by agitation in the wet way, shows even when greatly magnified no signs of crystals. It is peculiar that with the given relative proportions of sulphuret of potassium and mercury, the whole of the latter is not converted into cinnabar, but a small portion remains, in a very finely divided state, mixed with it; the mercury must not on this account be diminished in quantity: during the treat-

ment of the compound with water it is, owing to its much higher specific gravity, readily separated, and may be used for the next preparation. On account of this unavoidable loss, the yield of cinnabar instead of being, as calculation would make it, $9\frac{1}{4}$ parts from 8 of metal, is only 8 parts.

The concentrated solution of sulphuret of potassium first decanted from the precipitate and equalling the tersulphuret KS_3, may again be used for the same purpose, after boiling with sulphur to convert it into the pentasulphuret. During this boiling it deposits a small quantity of a black precipitate, which consists of a little sulphuret of mercury, dissolved by the tersulphuret of potassium.

Properties.—Cinnabar prepared by the moist way is a fiery red, soft, heavy, odourless, and tasteless powder, distinguishable from that prepared by sublimation, both by its bright colour and want of any crystalline appearance even when strongly magnified. Exposed to the light it gradually acquires on the surface a gray tint, arising from the separation of the mercury and sulphur, both of which in their free state remain in admixture with the compound. Cinnabar is insoluble in water, alcohol, cold nitric acid spec. grav. 1·2, cold hydrochloric acid, dilute sulphuric acid and acetic acid; hot nitric decomposes it, precipitating a portion of the sulphur, and converting the other portion into sulphuric acid, sulphate and nitrate of peroxide of mercury being formed; fuming nitric acid totally converts it into persulphate of mercury. Heated in a test tube it acquires nearly a black colour, and sublimes, without fusing, to a shining iron-gray mass, becoming red on rubbing; any adulterations in the cinnabar as *red lead*, *brick dust*, or *colcothar* remain behind. If this residue yields on charcoal before the blowpipe a bead of lead, red lead is present, but if it undergoes no change either brick dust or colcothar is present.

INULINUM.

Inuline.—Hellenine.

FORMULA: $C_{12}H_{10}O_{10}$ (?).

Preparation.—From Taraxacum root.—A quantity of dandelion root (that collected in the autumn is to be preferred), is shredded and digested with double its weight of water in a tin or copper vessel for 12 hours at nearly a boiling temperature, strained whilst hot through linen, the roots washed with a little warm water, well pressed, the liquor allowed to settle for some hours, the clear portion poured off, evaporated to about one-third the bulk of the water used for digestion, and placed in a porcelain or earthenware jar in a cool spot. After several days a considerable white deposit will be formed at the bottom of the vessel, which is collected on a filter, the supernatant liquor being poured off, and after evaporation to a syrupy consistence, again set in a cool place. This syrup which is now nearly solid will on diluting with cold water yield a white precipitate, which washed several times with cold water becomes perfectly white. The two deposits when drained are taken from the filter, spread on a porcelain tile and dried with a gentle heat. The yield will be about $\frac{1}{20}$ the weight of the fresh root.

By again boiling the root with water, a little more inuline is obtained, which, however, is not so pure as the first quantity.

For want of fresh dandelion root, that which has been dried may be used; this, however, does not yield so much or such pure inuline.

From dahlia roots, which also should be dug up in the autumn, it is better to prepare the inuline by the same process; or simply washing them with cold water (as in the preparation of starch), but

little inuline is obtained. There is no advantage in using the dahlia roots instead of the taraxacum.

Recapitulation.—Inuline exists in Taraxacum in a free state; the root contains in the autumn a much larger portion than in the spring or summer. On account of its slight solubility in cold water, the root must be digested in hot, but not boiling water; by boiling, a larger quantity of inuline would be obtained, but with it so much colouring and extractive matter as renders the purification difficult. The precipitate must not be dried on paper, otherwise it adheres to it so tightly as to be scarcely separable; nor must a high temperature be employed, as this causes a change in it.

Properties.—Pure dried inuline forms gray clear fragments, of a horny appearance, which yield on rubbing a perfectly white powder; it possesses neither taste nor smell. Strongly heated it is first converted into a kind of gum, becomes brown, then blackens, with the evolution of pungent vapours, and in the open air is entirely consumed. Cold water but slightly dissolves it (about $\frac{1}{500}$); on the other hand, hot water takes up more than its weight; the hot solution, unlike paste, is slimy, and on cooling precipitates most of the inuline as a powder. Iodine imparts to it a yellow, not a blue colour.

IODINUM BROMATUM.

Iodinii Bromidum.—Iodide of Bromine.—Bromide of Iodine.

FORMULA: $IBr_3 + xHO$.

Preparation.—(*a*) *With Bromine.*—1 Part of iodine is rubbed to a paste with 3 parts of water, poured into a narrow-necked flask capable of containing nearly 80 parts of water, 2 parts of bromine added,

and agitated until entirely dissolved, then diluted with water sufficient to bring the whole to 60 parts, filtered if necessary, and kept in a well-stoppered bottle, in a dark place.

(*b*) *With Bromide of potassium.*—3 Parts of powdered bromide of potassium and 1½ of peroxide of manganese are mixed and put into a glass flask, with a long narrow neck; a previously-cooled mixture of 4 parts of concentrated sulphuric acid and 4 of water are then added, and the neck of the flask is closed with a cork containing the shorter limb of a glass tube, doubly bent at right angles, the cork is surrounded with luting and bladder, the other limb of the tube passed to the bottom of a capacious glass vessel containing 1 part of iodine rubbed up with 3 of water, the receiver surrounded with cold water or snow, and the generating flask heated as long as red fumes are evolved. The dark brown solution is diluted with water to 60 parts (as in process (*a*)).

Recapitulation.—(*a*) Iodine and Bromine readily combine; in the proportions above given, 1:2, we obtain a deep brown solution (in which, to 1 at. of iodine, = 1586, a very little more than 3 at. of bromine, = 3000 parts, are present), which may be diluted with water as desirable; by filtration any impurities from the iodine are removed.

(*b*) When bromide of potassium, peroxide of manganese, and sulphuric acid are brought into contact, half the oxygen of the manganese, combining with the potassium forms potash, which with 2 at. of sulphuric acid is converted into bisulphate of potash; the protoxide of manganese formed combines with 1 at. sulphuric acid, and the bromine is evolved:—

1 at. KBr, 1 at. MnO_2, and 3 at. $SO_3 + HO$, form
1 at. $KO + 2SO_3 + HO$, 1 at. $MnO + SO_3$,
1 at. Br, and 2 at. HO.

1490 Parts of bromide of potassium require 545 of peroxide of manganese, and 1839 of hydrated sulphuric acid; rather more peroxide than this proportion is ordered, to allow for any impurities. 3 Parts of bromide of potassium yield 2 parts of bromine, consequently a bromide of iodine, of the same strength as under (*a*), is obtained.

Properties.—Concentrated bromide of iodine is a dark-brown fluid, bleaching litmus paper; of an extremely penetrating odour, and very volatile. Diluted as above directed, it is a dark yellow. It is distinguishable from chloride of iodine by its odour of bromine, by a deeper yellow colour when similarly diluted, but most accurately from its behaviour with chromate of potash and sulphuric acid, (*vide* HYDRARG. BROMID.), after the bromine and iodine are converted into bromide and iodide of potassium by shaking with caustic potash, evaporating, and heating to redness. Like solution of chlorine, when exposed to the light it decomposes water, oxygen being given off, whilst hydrobromic and hydriodic acids are formed.

IODINUM CHLORATUM.

Iodinii Chloridum.—Iodide of Chlorine.—Chloride of Iodine.

FORMULA: $ICl_3 + xHO$.

Preparation.—Chlorine evolved from a mixture of 1½ parts of common salt, 1½ parts of peroxide of manganese, 4 parts of concentrated sulphuric acid, and 4 of water, is conducted into a mixture of 1 part iodine and 3 water, and the brown liquid diluted to 60 parts.

Recapitulation.—The same may be said as in the previous article (*b*), excepting that, instead of a salt of potash, bisulphate of soda remains in the residue.

1½ Parts of salt contain not quite 1 part of chlorine, which bears the same proportion to 1 part of iodine as 3 at. Cl = 1329 to 1 at. iodine 1586.

Properties —Chloride of iodine closely resembles bromide of iodine, but smells more of chlorine, and when diluted has a paler yellow colour, &c.

KALIUM.

Potassium.

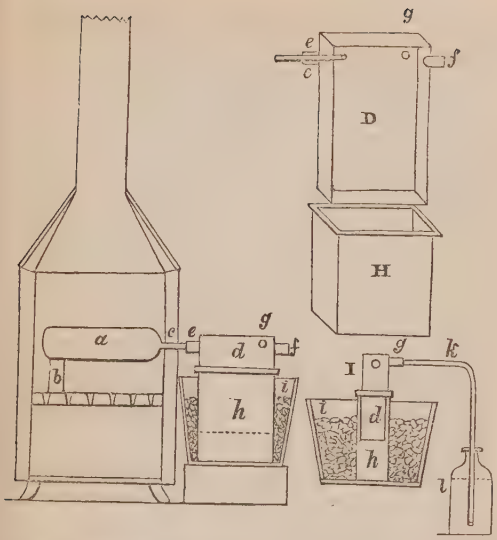
FORMULA: K.

Preparation. — Commercial cream of tartar is heated in a covered iron crucible so long as it gives off smoke and flame, when this ceases the crucible is removed, and, still covered, allowed to cool. 20 Parts of this ash (which should not, however, exceed 20 ounces) are finely powdered, mixed with 1 part of finely-powdered and 2 parts of coarsely-powdered (about the size of linseed) wood charcoal, and put into a wrought iron bottle, which has previously been covered about a ¼ of an inch thick with a mixture of 2 parts powdered Hessian crucible, 1 part of white bole, ¼ part of cowhair, mixed up to a pasty consistence with water, and applied in several even layers; about six inches of an ordinary musket barrel is then screwed into the opening of the bottle, and the lower portion surrounded with luting. The iron bottle is now placed horizontally in a wind furnace, and the hinder portion raised with a piece of brick to a level position, the weight of the front being supported by the tube, which must project, not more than two inches, through a hole in the side of the furnace; the opening is then luted round with clay. The receiver consists of two rectangular cases of copper plate, about 12 inches deep, 6 or 7 inches long, and 2 to 2½ inches wide, which shut into each other, the outer one being open

above and the inner one below. The inner prism has three perforations near the upper end, viz., 2 in the smaller sides exactly opposite each other, the first to admit the musket barrel, which must project about an inch into the vessel, the second being closed with a cork; the third perforation is in the broader side of the case, near the second one, and is also stopped with a cork, through which is passed a glass tube, bent downwards at right angles, and dipping into a bottle which is $\frac{2}{3}$ filled with mineral naptha. The exterior copper case is about $\frac{1}{4}$ filled with mineral naptha, and, after the inner one is fitted in it, placed in an earthen or iron vessel, having a perforation near the bottom of it, which is to be filled with ice. The gun barrel is to be luted into the aperture of the receiver with a mixture of oil and bole, and this may also be applied where the two copper cases join, to prevent the possibility of any water finding access and causing the inflamation of the potassium. The apparatus is exemplified as below:—

(*a*) is the iron bottle in the bed of the furnace, (*b*) the support at the further end, (*c*) the gun barrel, (*d*) the inner copper case, (*e*) the perforation to receive the musket barrel, (*f*) the perforation with the cork (this is used to pass the cleansing rod through), (*g*) is the perforation into which is fitted the glass tube, (*h*) the external copper case of the receiver, (*i*) the cooling vessel filled with ice, (*k*) the glass tube, (*l*) the glass bottle filled with mineral naptha, into which the glass tube dips. (D) the inner side view of the inner casing; (H) side view of the outer casing; (I) side view of the receiver on the smaller side, to show the fastening of the glass tube.

After the apparatus is thus arranged and the luting dry, the gun barrel and receiver being still disconnected, a fire is lighted in the furnace, commencing at the end farthest from the receiver; it



must be gentle at first, to drive off any adhering moisture, and not allow any of the powder to be carried with it; the furnace is gradually filled with fuel, so that the iron bottle becomes white hot, and this temperature is uniformly maintained during the process. As soon as the reduction of the charcoal commences, which is known by the appearance of greenish vapours in the interior of the iron bottle, the receiver is attached and fastened with oil luting, the cooler having previously been filled with ice. Together with the potassium a quantity of gas is given off, and passes through the glass tube and the naptha, into which the latter dips. By this stream

of gas, which must be neither too strong nor too feeble, the progress of the operation is judged. From time to time (that is, every 5 to 10 minutes), a long iron rod is introduced into the gun barrel through the perforation opposite (which is at other times closed with a cork), to ascertain whether it is stopped at all. If this is omitted, the gun barrel becomes gradually filled with a gray mass, and at last so much as effectually to close it, when nothing remains but to stop the process. The importance of attending to this is soon too plain to an operator. Of scarcely less importance is the cooling, for which water is insufficient, and ice must be used and renewed from above as it melts and escapes through the opening below. The progress or ending of the process may be judged from the cork-stopped aperture as well as the stream of gas; if, for instance, a circle of green flame is visible in the iron bottle, potassium is still coming over; if, on the other hand, this is not perceptible, and though the fire is a good one, no more gas is evolved on closing the aperture, the fire is allowed to go out. 20 Ounces of carbonized tartar require heating from 3 to 4 hours.

When the apparatus is thoroughly cool, the receiver is emptied into a deep porcelain dish, and after the carbonaceous and gray portions are picked out, tied up in a linen bag, placed in a dish of mineral naptha on a sand bath, heated to boiling, and the potassium squeezed out between the fingers, when it forms little shining globules, which on cooling must be preserved, together with that obtained pure at first, in mineral naptha, in a well-stoppered bottle. The potassium from 20 parts will equal 2 or 3.

Recapitulation.—On heating tartar (bitartrate of potash, $= KO + \bar{T}, HO + \bar{T}$) the tartaric acid decomposes, forming, besides several volatilized products (as paratartaric acid, formic acid, empyreumatic oil, car-

buretted hydrogen), carbonic acid, which combines with the potash. The oxygen and the hydrogen present in the water and acid are not sufficient to take up all the carbon, and as the oxygen of the air has scarcely any access to the heated mass, a great portion of the carbon remains, as such, intimately mixed with the newly formed carbonate of potash. This carbon, which from 20 parts of tartar will equal about 6 parts, is in the subsequent treatment, at a white heat, the reducing agent of the carbonate of potash, combined with the carbonic acid and oxygen of which it is evolved as carbonic oxide gas:—

1 at. $KO + CO_2$, and 2 at. C, form
1 at. K, and 3 at. CO.

865 Parts of carbonate of potash require, theoretically, for their entire reduction, not more than 150 parts of pure carbon; or, 14 parts of the former, (contained in 20 parts of tartar ash) scarcely $2\frac{1}{2}$ parts of the latter.

The evolved gas also contains some carburetted hydrogen, = CH, due to a small quantity of hydrogen which always remains combined with the carbon. The excess of carbon distributed through the mass is necessary to prevent the latter from fusing, and thus attacking and penetrating the iron vessel; as there is scarcely sufficient from the reduced tartar to ensure this, an extra portion is added, and also some coarser, to impart a certain porosity to the mass. The remainder of the process requires no further explanation.

The yield (2 to 3 parts from 20 parts of tartar ash, or 14 parts of carbonate of potash) bears no relation to the quantity of potassium contained in this salt. The reason of this great loss is partly due to imperfect reduction, and partly to the formation of a compound of carbonic oxide and potassium, $= 3K + 7CO$, which is evolved during the

process, together with the potassium, as thick gray vapours. A portion of this potassium and carbonic oxide condenses in the gun barrel with the potassium vapours, which, as well as a little charcoal mechanically carried over, cause its stoppage. The other portion of the carbonic oxide and potassium will be carried over into the receiver, and even into the glass tube and bottle connected with it. When this compound comes in contact with water or moisture, it gives rise to the formation of several products, which, however, have nothing to do with the formation of potassium. For instance, it decomposes water, evolves hydrogen, and becomes converted into a reddish salt, rhodizonate of potash = $3KO + C_7O_7$:—

1 at. $3K + 7CO$, and 3 at. HO, form
1 at. $3KO + C_7O_7$, and 3 at. H.

The rhodizonate of potash again separates into free potash, oxalate of potash, and croconate of potash :—

1 at. $3KO + C_7O_7$, forms
1 at. KO, 1 at. $KO + C_2O_3$, and 1 at. $KO + C_5O_4$.

Properties.—Potassium forms lustrous globules, resembling mercury, and of spec. grav. 0·865. At the ordinary temperature it is soft, and may be cut like wax ; it is entirely fluid far below the boiling point of water (at 120° Fah.), whilst at a red heat it boils and passes off in greenish vapours. If during the heating the air has had access, it ignites and burns, with a violet-red flame, to potash. Exposed to the air, at the ordinary temperature, it quickly becomes covered with a gray crust (the commencement of the oxidation), and is gradually converted into a slimy mass of caustic and carbonate of potash. In water it burns with violence, abstracting the oxygen, and liberating the hydrogen, which

accompanied by particles of potassium burns with a violet-red flame. Even under purified mineral naphtha, it gradually oxidizes (from the oxygen which is absorbed from the air by the naptha), becoming incrusted with potash.

KALIUM BROMATUM.

Potassii Bromidum.—Bromide of Potassium.

FORMULA: KBr.

Preparation.—(a) With caustic potash solution.—Freshly-prepared caustic potash solution, spec. grav. 1·333, is poured into a glass cylinder, and, during constant stirring with a glass rod, bromine is added in small portions, until the liquid acquires a permanent red colour. 7 Parts of caustic potash solution, of the above gravity, require 3 parts of bromine. The liquid is now evaporated to dryness in a porcelain dish, the residue finely powdered, intimately mixed with $\frac{1}{8}$ its weight of finely-pulverized wood charcoal, and the mixture added by spoonfuls to a red-hot iron crucible; when effloresced, it is heated to redness for about a $\frac{1}{4}$ of an hour, the crucible removed from the fire, and the contents poured out. The cooled mass is dissolved in double its weight of warm water, the solution filtered, and placed in a cool spot to crystallize. After 24 hours, the crystals formed are separated from the supernatant liquor, dried with a gentle heat, and the solution again evaporated to crystallization. The last portion of mother liquor, which reacts strongly alkaline, is evaporated to dryness and exhausted with hot alcohol, of 80 per ct. The yield from 3 parts bromine will be $4\frac{1}{2}$ parts.

(*b*) *With Bromide of iron.*—As under the article "FERR. BROM."; 2 parts of bromine, 2 of water and 1 of iron, are digested, filtered, the residue

washed with 2 parts of water, the solution warmed in a porcelain dish, and during agitation with a glass rod $1\frac{7}{10}$ of dry carbonate of potash are added. The turbid mixture should now possess a feebly acid reaction, but if after waiting some little time the blue litmus paper remains unchanged, and turmeric paper is rendered brown, a little more bromide of iron must be prepared and added, until the mixture acquires a faint acidity. Hereupon the whole is evaporated to dryness, the residue heated to redness for $\frac{1}{4}$ of an hour in an iron pot, then digested with water, filtered and evaporated to crystallization. The yield the same as under (*a*).

Recapitulation.—(*a*) When bromine comes in contact with a solution of caustic potash, the latter is immediately decomposed 6 at. of potash giving 5 at. of oxygen to 1 at. of bromine, which is thus converted into bromic acid, and uniting with the remaining atom of potash forms bromate of potash; the 5 at. of free potassium uniting with 5 other atoms of bromine to 5 at. of bromide of potassium:—

6 at. KO, and 6 at. Br, form
1 at. $KO + BrO_5$, and 5 at. KBr.

3540 Parts of potash or 13615 parts of potash solution, spec. grav. 1·333 (=26 per ct. pure potash) require 6000 parts of bromine. Considerable heat is evolved during the reaction, in consequence of which the bromine must be added gradually to the potash. So long as the liquid is warm the bromide of potassium remains dissolved, but the bromate of potash on account of its difficult solubility mostly separates as a white crystalline powder. The caustic potash solution must be freshly prepared, otherwise it will most likely contain carbonic acid which is but imperfectly driven off by the action of the bromine; to make sure that all the potash is combined with bromine, the latter is added in slight excess, a large excess is to be avoided as it is given off on evapo-

rating to dryness and wasted. To convert the bromate of potash into bromide of potassium, it is heated to redness with powdered charcoal, by this all the oxygen is abstracted and evolved as carbonic oxide :—

1 at. $KO + BrO_5$, and 6 at. C, form
1 at. KBr, and 6 at. CO.

2090 Parts of bromate of potash or 9540 parts of the dry saline mass (which contains 1 at. or 2090 parts of bromate of potash, and 5 at. = 7450 parts of bromide of potassium) require only 450 parts of carbon ; of common wood charcoal, more must of course be taken. The action of the carbon causes a slight deflagration, and occupies even with moderately large quantities but little time.

Commonly the bromate of potash is reduced by simply heating the saline residue to redness, or by passing sulphuretted hydrogen through its solution. Neither of these methods is to be recommended ; the first requires a long continued heat to drive off all the oxygen, and renders a portion of the bromide of potassium liable to be driven off. In the second method the hydrogen of the sulphuretted hydrogen combines with the oxygen of the bromate of potash, forming water, whilst sulphur precipitates :—

1 at. $KO + BrO_5$, and 6 at. HS, form
1 at. KBr, 6 at. HO, and 6 at. S.

At the same, time, however, a little sulphuric acid is formed, a portion of the bromic acid and sulphuretted hydrogen forming sulphate of potash, hydrobromic acid, and oxygen :

3 at. $KO + BrO_5$, and 3 at. HS, form
3 at. $KO + SO_3$, 3 at. HBr, and 6 at. O.

The liberated oxygen uniting with 2 at. of the precipitated sulphur to sulphuric acid now decomposes a fresh portion of bromate of potash, the acid of

which forms with a fresh atom of sulphuretted hydrogen sulphur, water and hydrobromic acid :—

6 at. O, 2 at. S. and 2 at. $KO + BrO_5$, form
2 at. $KO + SO_3$, and 2 at. BrO_5.
further
2 at. BrO_5, and 12 at. HS, form
12 at. S, 10 at. HO, and 2 at. HBr.

(*b*) Protobromide of iron and carbonate of potash are mutually decomposed, forming bromide of potassium and proto-carbonate of iron :

1 at. FeBr, and 1 at. $KO + CO_2$, form
1 at. KBr, and 1 at. $FeO + CO_2$.

1000 Parts of bromine (= 1350 parts of protobromide of iron) require 865 parts of carbonate of potash or 2 parts of bromine 1.7 parts of the latter. A portion of carbonic acid being evolved causes the effervescence. The reason why the mass possesses a feeble acid reaction, or in other words, why a very small portion of proto-bromide of iron should remain undecomposed, is to insure that no excess of alkali is present, and that a neutral salt shall be formed. By evaporating the turbid green mass, all the proto-carbonate of iron is converted into hydrated peroxide, and the latter as well as the slight excess of protobromide of iron, when heated to redness forms anhydrous peroxide, from which the bromide of potassium is separated by water.

Properties.—Bromide of potassium crystallizes in white cubes and octohedra, is permanent in the air, odourless, of a sharp saline afterwards cooling taste, resembling common salt. On heating it decrepitates like salt, and fuses to a clear liquid without decomposition ; in a strong red heat it volatilizes, although but slowly. It dissolves in 4 parts of cold and in its own weight of hot water ; it is soluble in 200 parts of cold alcohol of 80 per ct., and in 16 parts of boiling, the solutions have a neutral reaction. Its alkaline

reaction is due to adhering carbonate of potash, caused either by the use of caustic potash solution not free from the latter, or an excess of the potash solution; under these circumstances the salt becomes moist in the air, and effervesces with acid. On the addition of hydrochloric acid the salt should not become coloured, although chloride of potassium and hydrobromic acid are formed; if, however, it instantly acquires a reddish colour *bromate of potash* is present. The bromic and hydrobromic acids which are liberated at the some time, become mutually decomposed, forming water and bromine, which latter remains dissolved and occasions the colour :—

5 at. KBr, 1 at. KO + BrO_5, and 6 at. HCl, form
6 at. KCl, 1 at. HO, 5 at. HBr, and 1 at. BrO_5; further,
5 at. HBr, and 1 at. BrO_5, form
5 at. HO, and 6 at. Br.

Sulphuric acid is known by the white precipitate it causes with chloride of barium. *Chloride of potassium*, the most common impurity, cannot be detected by nitrate of silver, as chlorine and bromine are both precipitated by it, and the precipitates are soluble in caustic ammonia (that with bromine rather more difficultly). The best process is that given under the article "Hydrarg. Bromid," in which 2 at. of bromide of potassium react on 1 part of chromate of potash, and 3 at. of sulphuric acid. Lastly the contamination with *sulphuret of potassium* is to be considered; this occurs when caustic potash solution contains sulphate of potash, which on heating with carbon gives up its oxygen to the latter. Sulphate of iron causes in the solution of the salt a black precipitate of sulphuret of iron; by the cautious addition of protobromide of iron the sulphuret is removed; for

1 at. KS, and 1 at. FeBr, form
1 at. KBr, and 1 at. FeS.

KALIUM CYANATUM.

Potassii Cyanidum.—Cyanide of Potassium.

FORMULA: $K + C_2N = KCy$.

Preparation.—Into a capacious flask, which contains a layer of silver sand about an inch thick, are weighed 7 parts of water, and to this are gradually added, with continuous agitation, 3 parts of concentrated sulphuric acid; in another equally large flask is placed a filtered solution (prepared in the cold) of 2 parts of dried (not fused) caustic potash, in 10 parts of alcohol of 90 per ct.; the two flasks are connected with a double-limbed bent tube, one end of which is fitted, by means of a cork, so as to dip one inch into the neck of the first flask; the other limb dips to the bottom of the second flask, without being fixed in the neck; as soon as the acid mixture has cooled, 4 parts of finely-powdered yellow prussiate of potash are added to the acid, the cork quickly replaced, and the flask slowly heated in a sand bath until $\frac{1}{3}$ its contents have passed over into the second flask, which must be kept perfectly cool; when arrived at this point, the tube must be instantly withdrawn, or on the heat being removed absorption will take place. The white pasty mass in the receiving flask is quickly thrown on a filter, allowed to drain, then washed two or three times with alcohol of 90 per ct., pressed between filtering paper, dried as quickly as possible with a gentle heat, and kept in a well-closed bottle. The yield is about $1\frac{1}{2}$ parts.

Recapitulation.—Pure cyanide of potassium can be made only by direct combinations of pure prussic acid and pure potash. If we endeavour to obtain it by evaporating the solution, it becomes partially decomposed, evolves ammonia, and leaves

a residue of cyanide of potassium and formiate of potash :—

1 at. $K + C_2N$, and 4 at. HO, form
1 at. $KO + C_2HO_3$, and 1 at. NH_3.

If during the evaporation the air has free access, the potassium becomes oxidized, carbonate of ammonia is evolved, the residue consisting of cyanide of potassium and carbonate of potash :—

1 at. $K + C_2N$, 3 at. HO, and 2 at. O, form
1 at. $KO + CO_2$, and 1 at. $NH_3 + CO_2$.

We must therefore endeavour to bring the cyanide of potassium, as soon as formed, into an insoluble state, and this is most readily attained by passing a stream of hydrocyanic acid vapour into a spirituous solution of caustic potash ; cyanide of potassium, being but slightly soluble in spirits of wine, becoming less so the greater the strength of the latter. As caustic potash exerts a decomposing action on alcohol, especially when warm, the solution must be prepared only just as required, and also without heat ; and for the same reason it is to be well cooled during the transmission of the prussic acid. The formation of the prussic acid has been described under that article. 1920 Parts (4 ounces) of ferrocyanide of potassium form 311 parts (311 grains) of prussic acid, which represent $\frac{2}{3}$, or 300 parts of the cyanogen contained in the cyanide of potassium.

These 311 parts of hydrocyanic acid require 544 parts of pure potash to saturate it, for 1 at., $=337$ parts of prussic acid, forms, with 1 at., $=590$ parts of potash, 1 at. $=815$ parts of cyanide of potassium, and 1 at. $=112$ parts of water. The potash used for solution must not be the monohydrate, $=KO + HO$, as this has an instantaneous action on alcohol ; but potash obtained by evaporating its solution just to that point when a small portion

withdrawn on a rod solidifies on cooling. In this state it contains about 4 at. of water; consequently, for 311 parts of prussic acid, 960 parts of this potash are necessary; or, to 4 parts of prussiate of potash, nearly 2 parts; the slight excess of potash contained in these proportions is removed during the washing with alcohol.

The cyanide of potassium produced should be nearly 2 parts, but, owing to its partial solubility in alcohol, a certain portion is lost. In order to re-obtain the alcohol, it must be treated with proto-sulphate of iron (to fix the cyanogen), and then rectified.

The fused cyanide of potassium (see the following article) cannot be used as the source of the hydrocyanic acid, for, on decomposing it, carbonic acid will be liberated and contaminate the cyanide of potassium with carbonate of potash.

Properties.—Cyanide of potassium forms a snow-white crystalline powder, is odourless (but acquires in moist air the smell of bitter almonds), and of a pungent alkaline taste, with that of bitter almonds. It is deliquescent in the air, and in this state decomposes, giving off prussic acid, and becoming at last entirely carbonate of potash:—

1 at. KCy, 1 at. HO, and 1 at. CO_2, form
1 at. $KO + CO_2$, and 1 at. HCy.

If an aqueous solution of the salt is kept in a corked bottle, it gradually acquires a brown colour, and a dark brown matter separates, owing to the decomposition of the liberated prussic acid into soluble cyanide of ammonium and insoluble nitrogenized carbon:—

4 at. HCy, form
1 at. NH_4Cy, and 2 at. C_3N.

Heated it fuses (and if no air be admitted), without decomposition.

Any contamination with *iron* (ferrocyanide of

potassium) may be known by the addition of a solution of sulphate of copper, and treating the yellowish-gray precipitate thus obtained with hydrochloric acid, when, instead of becoming white and finally disappearing, it will acquire a reddish colour. It forms cyanide of copper and (chocolate-brown) ferrocyanide of copper (*vide* ACID. ACET.); the former of these is first reduced by the acid to white protocyanide of copper and then dissolved, whilst the latter remains unaltered, at least in the cold. If *carbonate of potash* is present it gives, with a solution of chloride of calcium, a white precipitate, soluble in acids, with effervescence. *Sulphate of potash* is detected by its precipitate with baryta salts, insoluble in free hydrochloric or nitric acids. To discover *chloride of potassium* the salt must be distilled with sulphuric acid, and the distillate tested as under prussic acid. It differs from the following preparation, in giving, when treated with dilute sulphuric acid, no carbonic acid.

KALIUM CYANATUM FUSUM.

Potassii Cyanidum Fusum.—Fused Cyanide of Potassium.

FORMULA: $7KCy + 3(KO + CyO)$.

Preparation.—8 Parts of yellow prussiate of potash are finely powdered, thoroughly dried with a gentle heat, intimately mixed with 3 parts of pure carbonate of potash, the mixture, thrown by spoonfuls into a red-hot Hessian or iron crucible, allowed to remain in the fire until thoroughly fluid and a glass rod or iron spatula dipped into it and withdrawn, becomes covered with a clear liquid, which on cooling solidifies to a white (not at all yellow) mass. When this point is attained, the crucible is removed from the fire, over which it is

held for a few minutes to allow the black particles swimming in it to subside the more readily; the clear liquid poured on a clean iron dish, broken into small pieces so soon as it has solidified, and kept in well-closed vessels. The yield will be from 6 to 6¾ parts.

Recapitulation.—Ferrocyanide of potassium, deprived of its water of crystallization, consists of $2KCy + FeCy$. By fusing this with an equivalent of carbonate of potash, the oxygen of half the potash combines with half the cyanogen of the cyanide of iron to cyanic acid, which, with the other half of the potash, forms cyanate of potash, $= KO + CyO$; the potassium liberated, with the other half of the cyanogen of the cyanide of iron, forms cyanide of potassium; the iron separates, in a metallic state, as grayish-black flakes, and the carbonic acid is evolved:—

2 at. $2KCy + FeCy$, and 2 at. $KO + CO_2$, form
5 at. KCy, 1 at. $KO + CyO$, 2 at. Fe, and 2 at. CO_2.

4610 Parts of anhydrous, or 5285 parts of crystallized (containing 3 at. of water) ferrocyanide of potassium require 1730 parts of carbonate of potash, which nearly agree with the proportions given: 8 and 3 parts. The above explanation of the process is not perfectly correct: for, instead of 5 at. of cyanide of potassium and 1 at. of cyanate of potash, I find that the salt has pretty constantly the formula, $7KCy + 3(KO + CyO)$.* The reason of it is most likely this, that the greater part of carbonic

* The portions of salt prepared at three different times gave, on precipitation with nitrate of silver, from 20 grains 26·4, 26·5, and 26·75 grains cyanide of silver, the mean = 26·55 grains. These 26·5 grains cyanide of silver correspond to 12·93 grains cyanide of potassium, consequently from 20 grains of the salt there remain 7·07 grains for cyanate of potash. The compound $7KCy + 3(KO + CyO)$ consists in 20 parts of 13·04 KCy and 6·96 $KO + CyO$.

acid liberated becomes deprived of half of its oxygen by a portion of the cyanide of potassium, and is consequently evolved as carbonic oxide. $1\frac{2}{3}$ Parts of every 2 at. of carbonic acid are thus reduced; (to avoid fractions we will suppose, at first 25 at. KCy and 5 at. KO + CyO are formed, and 10 at. of carbonic acid, of which 8 at. give up half their oxygen = 8 at. to 4 at. cyanide of potassium to form 4 at. cyanate of potash and 8 at. carbonic oxide:—

8 at. CO_2 and 4 at. KCy, form
4 at. KO + CyO and 8 at. CO.

Of the 25 at. KCy there remain 21 at.; and to the 5 at. KO + CyO 4 more are added, making 21 at., KCy and 9 at. KO + CyO, which stand in the relation to each other of 7 to 3. The oxygen of the air may also exert a partial oxidizing agency on the cyanide. Besides the products already mentioned, when the carbonate of potash or ferrocyanide of potassium is not thoroughly dry, ammonia is also formed (*vide* previous preparation), and being evolved on fusing, is detected by its odour.

The mixture must be added to the crucible by small quantities at the time, to allow of its being covered by the fused portion, as all which adheres to the sides of the crucible above this does not form a pure product. It is necessary to take care that no particles of iron remain floating in the mass previous to pouring it out.

8 Parts of prussiate of potash and 3 parts of carbonate of potash should produce more than 7 parts, but the yield is never so high as this, in consequence of a portion adhering to the crucible. To avoid wasting this, the crucible is well washed with cold water, filtered as quickly as possible, and the solution used to form other metallic cyanides, as cyanide of zinc, by adding to it a solution of sulphate of zinc, &c. It is seldom, however, that a solution of cyanide of potassium obtained in this manner is free

from iron; as the particles of this metal in the crucible abstract, during the digestion with water, a portion of the cyanogen from the cyanide of potassium and form with another portion of the latter ferrocyanide of potassium; the liberated potassium, by decomposing water and eliminating hydrogen, forming potash:—

3 at. KCy 1 at. Fe, and 1 at. HO, form
1 at. 2KCy + FeCy, 1 at. KO, and 1 at. H.

Properties.—The preparation just described forms solid white lumps of a crystalline fracture, odourless but possessing a strong alkaline taste like bitter almonds. In the air it deliquesces, evolving prussic acid and carbonate of ammonia, whilst carbonate of potash forms the residue. The prussic acid which separates is from the cyanide of potassium (see the previous article), and the carbonate of ammonia from the decomposition of the cyanate of potash:—

1 at. $KO + C_2NO$ and 3 at. HO, form
1 at. $KO + CO_2$ and 1 at. $NH_3 + CO_2$.

In closed vessels the aqueous solution behaves like that of the pure cyanide, *i.e.*, it acquires a brown colour and deposits a carbonaceous matter. Heated with dilute sulphuric acid it evolves hydrocyanic and carbonic acids (consequently when passed into lime water these gases cause a turbidness), and the residue will consist of sulphate of potash and sulphate of ammonia:—

1 at. $7KCy + 3\ (KO + C_2NO)$ 13 at. SO_3 and 19 at. HO, form
10 at. $KO + SO_3$, 3 at. $NH_4O + SO_3$,
7 at. HCy, and 6 at. CO_2.

Black specks in the mass will be *metallic iron*, from want of care in pouring it from the crucible, in which case its solution will generally have a slight yellow tinge (contains ferrocyanide of potassium) and gives a similar reaction, with sulphate of copper

as the previous preparation (when this is contaminated with iron). *Carbonate and sulphate of potash*, and *chloride potassium*, are also detected by the methods described p. 387.

KALIUM CYANATUM FERRATUM RUBRUM.

Potassii Ferridcyanidum.—Ferridcyanide of Potassium. —Red Prussiate of Potash.

FORMULA : $3KCy + Fe_2Cy_3$.

Preparation.—2 Parts of yellow prussiate of potash are dissolved in 20 parts of water ; chlorine is then generated from 3 parts of hydrochloric acid, spec. grav. 1·130 and 1 part of peroxide of manganese, and passed into the solution, until a small portion of it gives no blue colour or precipitate with persalts of iron, but only a brownish colour. The dark green and red solution is evaporated in a porcelain dish to $\frac{1}{4}$ its weight and allowed to crystallize ; the crystals, with the exception of the last portions which form and chiefly consist of chloride of potassium, are dried and kept in a closed bottle protected from the light. Their weight will be $1\frac{1}{2}$ parts.

Recapitulation.—When chlorine (for the formation of this gas from hydrochloric acid and peroxide of manganese see the article CHLORUM AQUOSUM) is passed into a solution of ferrocyanide of potassium, it detaches from 2 at. of the latter 1 at. of cyanide of potassium, with the potassium of which it combines, whilst the liberated cyanogen unites with the 2 at. cyanide of iron, and remains combined with the 3 at. of cyanide of potassium:—

2 at. $2KCy + FeCy + 3HO$ and 1 at. Cl, form
1 at. $3KCy + Fe_2Cy_3$, 1 at. KCl, and 3 at. HO.

5285 Parts of yellow prussiate of potash require 443

chlorine, which correspond to 455 parts of hydrochloric acid, and as during its evolution the manganese takes up half of the chlorine, so 910 parts of anhydrous or 3500 parts of hydrochloric acid, spec. grav. 1·130 (=26 p. ct. real acid) are requisite. This quantity of acid is, however, not sufficient, as the gas is never completely absorbed during its passage through the solution, and consequently nearly twice the calculated quantity of acid or for 2 parts of ferrocyanide of potassium, nearly 3 parts of hydrochloric acid (and 1 part of peroxide of manganese) are found to be necessary. Soon after the evolution of gas has commenced, the solution of the salt acquires a dark yellowish-green colour, becoming at last, by reflected light, almost opaque, though in transmitted light small quantities show a deep red. When arrived at this point a small portion must be frequently withdrawn on a glass rod and tested with a persalt of iron as directed. An excess of chlorine is to be avoided as much as possible, the salt already formed being in this case decomposed, whilst a blue compound separates. As long as a persalt of iron causes a blue precipitate in this solution, the latter contains ferrocyanide of potassium; if, however, it gives only a darker brown, the conversion is complete, and the chlorine must be immediately discontinued. The brown colour is occasioned by the conversion of the persalt of iron into percyanide of iron whilst its acid and oxygen unite themselves to the potassium:—

1 at. $3KCy + Fe_2Cy_3$, and 1 at. $Fe_2O_3 + 3SO_3$, form
3 at. $KO + SO_3$, and 2 at. Fe_2Cy_3.

The two atoms of percyanide of iron thus liberated remain dissolved, and occasion the brown colour. It is generally recommended to add a little caustic potash solution during the evaporation, to neutralize any slight excess of chlorine, as, with every

attention to the point at which all the yellow salt is converted into the red prussiate, this is generally present; and if this chlorine is not saturated it exerts a decomposing action, the last portion of crystals, if not those first formed, having a green or blue tint. This is certainly the case; but the addition of potash brings with it a still greater disadvantage, viz., that in the presence of a free alkali the ferridcyanide of potassium is again converted into ferrocyanide. The slightest excess of the potash again imparts to the liquid the property of giving a blue colour or precipitate, with persalts of iron. The last portion of the mother liquor gives a salt containing chloride of potassium, but the solution may be used as a re-agent. The salt must not be exposed to the action of the light, which causes in it, as in all ferruginous compounds corresponding to the oxide of iron, a partial reduction; the percyanide is converted, with the loss of cyanogen, into proto-cyanide, and the compound acquires the property of precipitating persalts of iron blue. This precaution is still more necessary with the solution.

Properties.—The ferridcyanide of potassium forms ruby-red rhombic prisms, as well as (in the last portions crystallized) yellowish-red or bronze-coloured needles; is odourless, and of a cooling saline taste, becoming metallic on the palate. Heated in a test tube, the crystals fly into extremely minute fragments, which fuse (but with difficulty) and, evolving cyanogen, leave a black residue, consisting of cyanide of potassium and paracyanide of iron (iron with less cyanogen than $FeCy$). It dissolves in 3½ parts of cold, and less than 2 parts of boiling water, but not in alcohol: the solution has a neutral reaction. Any contamination with *ferrocyanide* is detected by the blue colour persalts of iron cause in its solution. (*Vide* ACID. ACET.)

KALIUM CYANATUM SULPHURATUM.

Potassii Sulphocyanidum.—Potassæ Sulpho-Hydrocyanas.—Sulphocyanide of Potassium.

FORMULA: $K + CyS_2$.

Preparation.—8 Parts of ferrocyanide of potassium are rubbed to a fine powder, thoroughly dried, mixed with 3 parts of carbonate of potash and 6 parts of sulphur; the whole of the mixture is placed in a Hessian crucible, at a low red heat, which is then covered, and when the mass has fused to a clear liquid, the heat continued for a quarter of an hour, and the fluid poured on a clean iron plate. The black mass thus obtained is powdered, and digested with six times its bulk of spirits of wine of 80 per ct. for some hours, then filtered and the residue washed with more alcohol. The alcohol is distilled from the solution, the remaining salt dissolved in water and crystallized. The crystals are dried as quickly as possible with a gentle heat and kept in well closed vessels. The product should be 8 parts.

Recapitulation.—On fusing anhydrous ferrocyanide of potassium, carbonate of potash and sulphur together, sulphocyanide of potassium and sulphuret of iron are formed whilst the carbonic acid and oxygen of the potash (as sulphurous acid) are evolved:—

2 at. $2\,KCy + FeCy_3$, $2KO + CO_2$, and 17 at. S, form 6 at. $KCyS_2$, 2 at. FeS_2, 2 at. CO_2, and 1 at. SO_2.

4610 Parts of dry or 5285 parts of crystallized ferrocyanide of potassium require 1780 parts of carbonate of potash, and 3400 parts of sulphur. Alcohol abstracts only the pure sulphocyanide of potassium, whilst the sulphuret of iron, any undecomposed ferrocyanide of potassium, carbonate of potash, or excess of sulphur remain.

8 Parts of crystallized prussiate of potash should,

by calculation, yield 9 parts; the loss is due to absorption by the porous crucible.

Properties.—Sulphocyanide of potassium forms colourless and odourless crystals, which in form and taste resemble nitre, they deliquesce in the air. It is rather less soluble in alcohol than in water; its solutions have a neutral reaction. The great depression of temperature caused in dissolving this salt is worthy of notice. With persalts of iron it forms a blood-red liquid (*vide* BISM. NITR.); if it contains *ferrocyanide of potassium* the blue coloration or precipitate will also be present, (ACID ACETIC).

KALIUM IODATUM.

Potassii Iodidum.—Iodide of Potassium.—Hydriodate of Potash.

FORMULA: KI.

Preparation. — After carefully testing all the methods recommended for the preparation of this compound, I give the preference to the process resembling that given under the article "KALIUM BROMATUM;" it is as follows:

(*a*) To freshly prepared solution of caustic potash spec. grav. 1·333, in a cylindrical glass vessel, dry iodine is added, with constant stirring, and without the application of heat, until the solution acquires a brownish-yellow colour, and retains it when allowed to stand some hours. To 4 parts of caustic potash of the above spec. grav. 3 parts of iodine will be requisite. The solution and any precipitate that may have formed, are now poured into a porcelain dish evaporated to dryness, finely powdered, then intimately mixed with ½ its weight of well powdered wood charcoal and the mixture projected by spoon-

fuls into a red hot iron crucible; the heat is continued for a quarter of an hour, and the crucible emptied into some iron vessel. The cooled mass and the portions adhering to the crucible are treated with their weight of water in a porcelain dish, and the solution aided by heat; the liquid is then filtered and evaporated slowly to crystallization, which is repeated with the mother liquors, until they are reduced to a small quantity. The crystals are drained from the mother liquor in a funnel, thoroughly dried on a flat dish, and kept in a well-closed bottle. 3 Parts of iodine yield nearly 4 parts.

The last of the mother liquor generally reacting strongly alkaline, is treated, if of sufficient quantity, with alcohol of 80 per ct., which leaves the carbonate of potash.

(*b*) Iodide of iron as described under the article FERRUM IODATUM, is formed with 4 parts of iodine, 8 of water, and 1 of iron, then filtered and the residue washed with 4 parts of water. The filtered solution is poured into a porcelain dish, and $2\frac{1}{6}$ parts of carbonate of potash gradually added during constant stirring; the mass which has still a feebly acid reaction, is evaporated to dryness, and heated to redness in a cast-iron pan for $\frac{1}{4}$ of an hour; when cool, it is exhausted with water, and the clear solution crystallized. The yield is over 5 parts.

Recapitulation. (*a*)—Just as in the formation of bromide of potassium :—

6 at. KO, and 6 at. I, form
1 at. KO + IO_5, and 5 at. KI.

3540 Parts of potash or 13615 of potash solution, spec. grav. 1·333 require, 9516 parts of iodine, or 4 parts of solution nearly 3 parts of iodine, and as a slight excess of the latter is requisite, 3 parts are necessary. The caustic potash solution must of course be freshly prepared and pure. It is heated to redness with charcoal for the same reason as

bromide of potassium, viz. to facilitate the decomposition of the iodate of potash:—

1 at. $KO + IO_5$, and 6 at. C, form
1 at. KI, and 6 at. CO.

2676 Parts of iodate of potash or 13056 parts of the dry saline mass require only 450 parts of charcoal, but on account of the impurity of the latter, the quantity is doubled.

(*b*) This process also corresponds exactly with that for bromide of potassium:—

1 at. FeI, and 1 at. $KO + CO_2$,
1 at KI, and 1 at. $FeO + CO_2$.

1586 Parts of iodine (=1936 parts of proto-iodide of iron), require 865 parts of carbonate of potash, or 4 parts of iodine $2\frac{1}{9}$ parts of the latter. The slight excess of iodide of iron is decomposed on heating.

Properties.—Iodide of potassium crystallizes in white cubes and octohedrons,* which are odourless and of a pungent saline, afterwards slightly bitter taste. In a dry atmosphere it remains unchanged; but in damp air the crystals gradually become yellow and moist, from the carbonic acid and water in the air acting on them, causing the formation of carbonate of potash and hydriodic acid; the latter is again decomposed by the oxygen of the air into water and iodine:—

1 at. KI, 1 at. CO_2, and 1 at. HO, form
1 at. $KO + CO_2$, and 1 at. HI.
1 at. HI, and 1 at. O, form
1 at. HO, and 1 at. I.

If the salt contains a small portion of carbonate of potash, it gradually attracts moisture from the air,

* In commerce the opaque porcelain-looking crystals are preferred; the method of obtaining these appears to be by allowing them to form in a warm solution. The evaporation of course, in this case, must proceed but slowly.

becoming entirely liquid; the exterior portion of carbonate of potash attracting the moisture forms a medium of solution for a portion of the iodide of potassium, and this continues layer by layer throughout the crystal. At a red heat the salt fuses without decomposing, although slight traces of it volatilize. It requires $\frac{3}{4}$ its weight of cold and only $\frac{1}{2}$ of hot water for its solution. Alcohol of 80 per ct. dissolves in the cold $\frac{1}{7}$, when heated $\frac{1}{3}$ its weight; the solutions must not render turmeric paper brown. *Carbonate*, *sulphate*, or *iodate of potash* and *sulphuret of potassium*, are detected as under bromide of potassium. If *iodate* is present, hydrochloric acid instantly causes a brown colour; it is to be borne in mind that this brown colour may also be developed with *pure iodide of potassium, after several hours*, owing to the free hydriodic acid becoming decomposed by the oxygen of the air into water and iodine. *Chloride of potassium* is detected by entirely precipitating a small portion of the salt with nitrate of silver, agitating the precipitate with caustic ammonia, filtering and supersaturating the filtrate with nitric acid. The nitrate of silver precipitates both the chlorine and iodine; the first compound is readily soluble in caustic ammonia, that with iodine is not so; on supersaturating with nitric acid, which abstracts the solvent, the chloride of silver again precipitates. In this experiment the ammonia and nitric acid must both of course be entirely free from chlorine.

KALIUM OXIDATUM HYDRATICUM.

Potassæ Hydras.—Potassium Causticum.—Caustic Potash.

FORMULA OF THE FUSED: KO + HO.
FORMULA OF THE DRIED: KO + xHO(3—4HO).
FORMULA OF THE LIQUID: KO + xHO(13HO).

Preparation.—1 Part of carbonate of potash is

dissolved in 10 parts of water in a silver or iron pot, the solution is brought to the boiling point, and whilst constantly stirring with a silver or iron spatula, 1 part of freshly hydrated lime is gradually added; the boiling is then continued for a quarter of an hour, a small portion filtered and poured into dilute sulphuric acid; if any gas bubbles are given off (carbonic acid evolved), a few spoonfuls more of hydrate of lime are added, and after some minutes the test with acid is repeated. The second testing is seldom necessary, as the first quantity of lime is generally found to have abstracted all the carbonic acid from the potash. The whole of the contents of the pot is now quickly thrown on a strong bleached linen cloth, strained over a deep iron vessel, the liquor is returned until it runs through clear (which, as the chalk forms a good filtering medium, soon occurs), and is then put into vessels with glass stoppers. When no more liquid drops, the strainer is put with its contents into a pot, in which are 8 parts of pure water, the whole is warmed and strained through the linen bag with the precautions before mentioned. The clear liquors are quickly evaporated in the cleansed iron pot until they attain, when cool, a spec. grav. of 1·333, which occurs when it is reduced to 2 parts. The pot is now removed from the fire, and the contents poured into a bottle having a glass stopper; when thoroughly cool the spec. grav. is again taken, and if found to be more than 1·333, is reduced to this with distilled water; the liquid now constitutes liquor potassæ or caustic solution of potash.

To obtain *dry caustic potash* the above liquid is evaporated in an iron pot until a drop removed on the end of the stirring rod solidifies on cooling; it is then poured on a clean sheet of iron, quickly broken up and enclosed in a wide-mouthed bottle.

The fused potash (*Caustic, Hydrate of Potash, Lapis Causticus,*) is formed when the solution, evapo-

rated to the point just mentioned, is poured into a silver or iron crucible, (taking care the latter is only half filled,) and heated until it no longer froths up but fuses quietly, it is then cast in iron moulds like lunar caustic, and the sticks as soon as cold put in a well-closed bottle.

1 Part of carbonate of potash forms rather more than 2 parts of liquor potassæ, spec. grav. 1·333; $\frac{5}{6}$ part of Dry or $\frac{2}{3}$ part of Fused Potash.

Its separation by alcohol from sulphate, carbonate, and all other substances insoluble in this agent, as ordered in the French pharmacopœia is altogether objectionable. If, for instance, the alcohol is distilled from this solution in a glass retort, the glass becomes acted on, the potash is contaminated with silica, and acquires a yellow colour, owing to the action of the potash on the alcohol. If the last trace of alcohol is driven off in a silver crucible the colour rises to the surface as a black scum, and can be taken off, but at the same time the action of the potash on the carbon gives rise to carbonic acid, and thus the preparation "Potasse à l'alcohol" contains carbonate of potash.

Recapitulation.—Carbonate of potash, in diluted solution readily yields up its acid to lime, which thus combined, precipitates as insoluble carbonate of lime:—

1 at. $KO + CO_2$ and 1 at. CaO, form
1 at. KO and 1 at. $CaO + CO_2$.

865 Parts of carbonate of potash require only 463 parts of hydrate of lime ($CaO + HO$); but the quantity of lime must be increased, as it is never entirely pure, and it also serves to keep the shape of the filter whilst straining the solution. There is no fear that lime will be found in the solution. The decomposition takes place also in the cold, but only after a longer period; in order that it may be complete, the solution must not be too concentrated, as

in this case the lime will not abstract the carbonic acid, on the contrary, strong caustic potash dispossesses carbonate of lime of its acid, becoming converted into carbonate of potash. A silver vessel is the best to boil it in, otherwise a clean iron one may be used, but neither porcelain, copper, nor any other metal is applicable, from the action the potash exerts on them. For the same reasons no wooden or porcelain stirrer should be used, and the strainer must be made of bleached linen. If all these things are attended to a colourless solution is obtained, which when concentrated bears scarcely a yellow tinge. In testing the solution for carbonate of potash, the precaution must be taken to pour the filtered solution into a large excess of acid, and not the acid to the solution, as in the latter case no gas is evolved until all of it has combined with the potash to form bicarbonate. Lime water, which is also one of the tests generally given for detecting carbonate of potash in the solution, is inapplicable for the purpose, as in solutions perfectly free from carbonic acid it causes a precipitate (hydrate of lime). The best and quickest method of separating the carbonate and caustic lime is to strain it; by allowing it to settle and decanting the clear liquor a great deal of time is lost, which, from the avidity with which the solution absorbs carbonic acid, must be circumscribed as much as possible. With no other preparation are quickness and cleanliness in manipulation more requisite than with caustic potash.

The pasty lime mass, after its second exhaustion, contains without doubt more potash, but the quantity is too small to requite the expense of evaporating a third washing. Water may however be passed through the filter to serve for other purposes.

Properties.—Pure caustic potash is a colourless or slightly yellow oily-like fluid of a feeble peculiar smell and an excessively caustic corrosive taste. A brownish colour is due to *organic matter*,

Having a spec. grav. 1·333 it contains in 100 parts 26·3 parts potash 73·7 parts water. The proportion of water in the dry preparation varies with the length of time it remains on the fire, generally it is between 36 and 44 per ct.; the water of hydration in the fused is constant at 16 per ct. Both the latter form solid masses white, or with a slight yellow tinge, of a crystalline fracture; in the air it attracts water and carbonic acid, deliquesces, and like the liquor potassæ becomes a solution of carbonate of potash. A slight trace of *carbonic acid* is almost always found in this preparation, and though an impurity, is in most cases too slight to be of consequence. If on agitating with alcohol it forms a very turbid solution, this is due, supposing acids cause but a slight effervescence, to other bodies insoluble in this menstruum, as *sulphate* and *silicate of potash; chloride of potassium*, &c., owing to the carbonate of potash used being impure. It is worthy of remark here, that caustic potash of spec. grav. 1·333 does not dissolve even a trace of sulphate of potash, all of which salt becomes deposited, and may be separated by decantation so soon as the solution attains this gravity. It is also detected in a potash solution after saturation with nitric acid, by the addition of chloride of barium causing a white precipitate; in the same way chloride of potassium is determined by nitrate of silver. If on saturating the solution with nitric acid, white flocculent matter separates, it will be *silicic acid;* without this separation silicic acid may be present, as this substance in a hydrated state or until it has been dried, is capable of slight solution in water and acids. For this reason the liquid is evaporated to dryness, and the residue treated with water, when any turbidness will arise from silica. Any white turbidness caused by solution of ammonia in the solution, supersaturated with nitric acid, is from *alumina*, and if sulphocyanide of potassium imparts

a red colour, *iron* is present (*vide* BISMUTH NITR.). This latter body is also detected in potash by the direct application of sulphide of ammonium, when a black precipitate is formed, which immediately disappears on the addition of hydrochloric acid; if, after this, any black particles remain suspended in the liquid, they are filtered off, dissolved in nitric acid and ferrocyanide of potassium added to the solution, when, if a chocolate precipitate is deposited, *copper* is present (*vide* ACID. ACET.). Oxalate of ammonia is added to the newly saturated solution, to determine whether *lime* is present, and to the liquid filtered from the oxalate of lime (if any is formed) phosphate of ammonia is added, to detect *magnesia* (*vide* CALC. CHLOR.). Traces only of iron, copper, lime or magnesia can occur in caustic potash solution; generally these substances are considered as totally insoluble in it, but this is not quite correct.

KALIUM OXIDATUM ACETICUM.

Potassæ Acetas.—Acetate of Potash.

FORMULA: $KO + \bar{A}$.

Preparation.—(*a.*) *With Acetic Acid.* A beaker glass is not more than half filled with a weighed quantity of pure acetic acid, to which is added in small portions, and with constant stirring, dry carbonate of potash, until the acid reaction and all effervescence disappear. 2 Parts of acid, spec. grav. 1·045, require 1 part of carbonate of potash. The acid reaction is again slightly restored by acetic acid, the liquid filtered, if necessary, and evaporated in a porcelain dish, at first over an open fire, but afterwards, when it has acquired a thickish consistence, on a sand bath, (a little acetic acid being occasionally added,) to dryness. The salt while

warm is transferred to well-closed bottles. The product is about $1\frac{1}{2}$ parts. If this salt is prepared in large quantities a clean copper pan will do to boil it in, taking care that it is not allowed to cool in it, and that the vessel is emptied as soon as a pellicle forms, as the salt should be dried in a porcelain dish.

(*b.*) With acetate of lead the preparation may be made as cheaply, with the advantage of the carbonate of lead as a secondary product. The following method is then followed: a certain quantity of sugar of lead is dissolved in six times its weight of pure water, and carbonate of potash, dissolved in twice its weight of water, added so long as a precipitate forms. 9 Parts of sugar of lead require $3\frac{1}{2}$ of pure carbonate of potash. After subsidation, the supernatant liquor is decanted, the residue thrown on a straining cloth covered with filtering paper, then washed with water, and the liquors mixed together are evaporated in a porcelain dish (if the quantity is large, in a clean copper vessel) to about the weight of the acetate of lead used, allowed to cool, and sulphuretted hydrogen gas passed through it. If, after standing some time, a small portion withdrawn experiences no change, by sulphuretted hydrogen, the liquid is filtered from the black precipitate, (if necessary it must again be treated with sulphuretted hydrogen, this however is seldom requisite,) the filtrate supersaturated with acetic acid, and evaporated as directed under (*a.*). From $4\frac{1}{2}$ to $4\frac{3}{4}$ parts of pure acetate of potash should be obtained.

Recapitulation.—The acetic acid drives off the carbonic acid, and combines with the potash:—

1 at. $KO + CO_2$, and 1 at. $\bar{A}$, form

1 at. $KO + \bar{A}$, and 1 at. CO_2.

865 Parts of pure carbonate of potash require 638 parts of anhydrous acetic acid, or 1772 parts,

spec. grav. 1·045 (containing 64 per ct. water) for saturation. As, however, during the evaporation a small portion of the acid is evolved, this must be slightly in excess, and towards the end of the process renewed from time to time. Clean copper is not acted upon by the boiling solution, and vessels of this metal may thus be substituted for porcelain during concentration, as economising fuel, but they must not be used to bring the salt to dryness, as, on account of the readiness with which the metal conducts heat, the salt is liable, by becoming too hot, to be partially decomposed, and acquire a gray colour; at the higher temperature also copper is liable to be acted on by acetate of potash. On account of the avidity with which it absorbs water, it must be put, whilst still warm, into closed vessels; if heated after it is dry, even in porcelain, it acquires a higher temperature, and although nothing more evaporates, a portion of the acid decomposes, and, owing to the separation of carbon, the salt acquires a gray colour.

(*b.*) Sugar of lead has already, under several preparations, been stated to be a compound of 1 at. oxide of lead, 1 at. acetic acid, and 3 at. of water; from this, carbonate of potash precipitates the oxide of lead as a carbonate; the potash uniting with the acetic acid:—

1 at. $PbO + \bar{A} + 3HO$, and 1 at. $KO + CO_2$, form
1 at. $KO + \bar{A}$, 1 at. $PbO + CO_2$, and 3 at. HO.

2370 Parts of sugar of lead require 865 parts of carbonate of potash. After all the acetate of lead is decomposed, traces of that metal still remain in solution; to entirely separate them, the liquor is concentrated, and treated with sulphuretted hydrogen, of which only very little is requisite. As an excess of carbonate of potash is used to precipitate the liquid, the alkaline reaction is, after separating

the sulphuret of lead, and previous to its evaporation to dryness, neutralized with pure acetic acid.

The carbonate of lead from 9 parts of acetate will equal 6 parts.

Properties.—Acetate of potash forms a snow-white powder, consisting of scales having a satiny lustre, of a feeble odour of acetic acid, and pungent saline taste. In the air it quickly attracts moisture, and deliquesces. Heated it fuses, giving off more or less decomposed acetic acid, empyreumatic oil, &c., and yielding finally a black residue, which is a mixture of carbonate of potash and carbon. In water and alcohol it dissolves with the greatest readiness; the solutions have a neutral reaction; the aqueous solution does not long remain so, becoming covered with mildew, and the acetate converted into carbonate. The simplest explanation of this change is that 1 at. of acetic acid attracting 8 at. of oxygen from the air, forms 3 at. of water and 4 at. of carbonic acid, 1 at. of which combines with the potash:—

1 at. $KO + C_4H_3O_3$, and 8 at. O, form
3 at. HO, 3 at. CO_2, and 1 at. $KO + CO_2$.

That the process is in reality not nearly so simple, is proved by the vegetable matter (mouldiness) which makes its appearance. The most probable impurities in this preparation are *carbonate of potash*, (if the acid was not in excess during evaporation), *sulphate of potash*, *chloride of potassium*, *alumina*, *lime*, *magnesia*, *iron*, *lead*, *copper*, *tin*, which may respectively be detected by hydrochloric acid, nitrate of baryta, acetate of silver, ammonia, oxalate of ammonia, phosphate of ammonia, sulphocyanide of potassium, sulphuric acid, sulphuretted hydrogen, ferrocyanide of potassium, and chloride of gold (*vide* ACIDUM ACETICUM, and KALIUM OXIDATUM).

KALIUM OXIDATUM CARBONICUM.

Potassæ Carbonas.—Carbonate of Potash.—Salt of Tartar.

FORMULA: $KO + CO_2$.

Preparation.—There are several varieties of this salt, differing in their state of purity; purified, pure, and chemically pure.

(*a.*) *Purified.* (*Kalium Carbonicum Depuratum*). 1 Part of common potashes (the Hungarian are to be preferred) are warmed in an iron pot with 2 parts of water, until all the solid lumps are softened, the whole is then transferred to a glazed stone vessel, and allowed to remain quietly for two days in a cool spot, then strained into an iron pot, through filtering paper laid on a linen cloth, on which the precipitate is afterwards thrown. As soon as all the liquor has drained off, it is evaporated, without washing the contents of the strainer, in a clean iron vessel, until a pellicle forms, then again placed in the earthen vessel, and allowed to remain for a few days in a cool spot. The salt which separates is collected on a linen strainer, and washed once or twice with a very little cold water; the solutions which filter off are then mixed, and evaporated to dryness in a clean iron pan, stirring constantly towards the end of the process with an iron spatula. The dry salt is again dissolved in half its weight of water, the solution allowed to subside, after a couple of days poured off the residue, and this, if bulky, is washed with a little cold water, the liquid evaporated to dryness, and the salt put, whilst warm, into well-closed bottles. The product, of course, depends on the quantity of impurities in the common potash, and will vary from 60 to 90 parts in 100 potash.

(*b.*) *The pure salt.* This is generally made by

heating the purified cream of tartar to redness. Of course in this process all the acid of this salt is lost, half of it may be saved by following the directions given under the article ACIDUM TARTARICUM, viz.: combining it with lime, and decomposing the salt thus formed with sulphuric acid. For this purpose 25 parts of cream of tartar, 150 of distilled water, and 5 of hydrate of lime, are digested for some hours at a gentle heat, allowed to cool and subside, then filtered, and after washing the residue with distilled water, the mixed liquors are evaporated in a clean iron vessel to dryness. A cast-iron dish is $\frac{4}{5}$ filled with the dry salt, covered with an iron top, placed in a good furnace, surrounded with coal, and heated until neither smoke nor flame escapes from it. Whilst heating it, the mass must occasionally be moved about with an iron spatula. When the whole mass acquires a red heat, and a small portion withdrawn dissolves in water without colouring it, while the charcoal subsides, the vessel is removed from the fire, its contents transferred to an iron pot, the crucible again filled with tartrate, and burnt, and this repeated until the whole is finished. The carbonaceous masses are then coarsely powdered, boiled with four times their weight of distilled water in a clean iron vessel, strained through linen; the boiling twice again repeated with fresh water, the liquid allowed to deposit in glass bottles, filtered, and evaporated to dryness in clean iron vessels. The salt, whilst warm, should be transferred to well-closed bottles. 100 Parts of purified cream of tartar yield 34—36 parts of carbonate of potash.

Instead of the purified, common tartar may be used, it is heated alone to redness, and 100 parts yield about 24. Nevertheless I must remark that this potash is frequently (not always) contaminated with cyanogen.

Formerly saltpetre was always added, in order to

deflagrate the cream of tartar. This method is objectionable for several reasons; in the first place it is impossible to determine the exact quantity of nitre that will be requisite: if too little is used a yellow or brownish solution results, whilst with too much the product is contaminated with nitrate or nitrite of potash; secondly, the carbonate of potash is very liable to contain cyanogen (if the common tartar has been used this is always the case). Thirdly, even allowing the superiority of the method, the cost of it will be too great, as to retain the purity of the product, chemically pure nitre must be used.

(*c*) *Chemically pure.* Sometimes the carbonate of potash obtained from cream of tartar is chemically pure, but should this not be the case, the following method must be resorted to. A certain quantity of carbonate of potash, (that prepared from potash will serve, if it does not contain too much sulphate or chloride,) is dissolved in its weight of water, and sufficient acetic acid gradually added, to give it an acid reaction. (Acetic acid not quite free from empyreumatic matter may be advantageously employed.) From the acid solution any sulphate is precipitated by a concentrated solution of acetate of baryta; as soon as the sulphate of baryta has thoroughly subsided, the liquid is filtered, and acetate of silver (which, as it requires a very large quantity of water for its solution is only rubbed to a fine pulp with water) added to precipitate the chlorine; the chloride of silver is then removed by filtration. Too large a portion of the acetates of baryta and silver is if possible avoided, any excess being only wasted.

The clear liquor after separation from both precipitates is evaporated to dryness in a porcelain vessel, the salt thrown by spoonfuls into a red hot iron dish, taking care not to add a fresh portion until the previous one has ceased to puff up, the whole heated to redness, and when neither smoke nor flame appears the dish is allowed to cool a little, and then

emptied. The gray mass is coarsely powdered, boiled in an iron vessel with distilled water, and the process (*b*) followed.

Recapitulation. (*a*)—The common potashes are an impure carbonate of potash contaminated with sulphate of potash, chloride of potassium, silica, and also, generally, though in small quantities, with alumina, lime, magnesia, iron, copper, manganese, chromium, soda, and phosphoric acid, together with occasional admixture of sand, common salt, &c. There are several different kinds met with in commerce, but on account of its greater purity the Hungarian is to be preferred, the Russian is also tolerably pure, and preferable to the German. On treating the potash with 1½ to 2 parts of hot water, there are dissolved, besides the carbonate of potash, the sulphate, chloride of potassium, and a part of the silica, as well as any soda and alkaline phosphates which may be present; whilst most of the silica partly combined with potash, together with the other impurities (as hydrated oxides, carbonates, and phosphates) remain behind. It must not pass unnoticed that small traces of lime, magnesia, iron, manganese, chromium, as well as alumina and copper if present, remain dissolved and are partially but not entirely separated on again evaporating to dryness. Hot water is preferable to cold, as it acts on the potashes more readily and completely. On standing several days in a cool place, the solution deposits all the insoluble matter, and if the sulphate of potash is present in any quantity a portion of it crystallizes out. The clear solution still contains most of the sulphate of potash, and all the chloride of potassium, together with the silica, &c. To remove the greater part of the sulphate, the solution is evaporated to a pellicle, allowed to stand some days, and then strained. The solution yet contains some sulphate of potash, chloride of potassium and silica, which by evaporating to dryness, and dis-

solving in as little cold water as possible, is partially removed. In this way a salt sufficiently pure for most purposes may be made, but it cannot be obtained perfectly pure by this method. In evaporating, no other than an iron or silver vessel should be made use of, whilst wooden bowls, spatulas, &c., are to be avoided, as from the action of the salt on them it acquires a yellow colour.

The residue from the first, second, and third straining is thrown into a leaden cistern, covered with water, the adhering carbonate of potash neutralized with sulphuric acid, and the residue purified as sulphate of potash.

(*b*) The recapitulation of the process of burning cream of tartar (bitartrate of potash) has already been gone through under the article KALIUM. On evaporating to dryness, and burning the solution of neutral tartrate of potash, obtained on saturating the bitartrate of potash with lime, the product is the same. One peculiarity of this process is the separation of ammonia; this is perceptible on removing the carbonaceous mass whilst red hot, from the crucible, and evidently arises from the condensation and combination of its constituents, hydrogen and nitrogen, in the pores of the charcoal. If common tartar is employed cyanogen is frequently formed, and is due to the nitrogenised substances which separated with it from the grape juice; the nitrogen combining with a portion of carbon forms cyanogen, and this unites with the metal of a part of the potash, whilst the oxygen of the latter combines with another portion of carbon. The heated mass consists of a mixture of carbonate of potash, carbon, and a little carbonate of lime (also traces of different metals); on treating with water the carbonate of potash dissolves, whilst the other substances remain behind. If the cream of tartar contains chloride of potassium, this, with cyanide of potassium and traces of iron and lime, will be found in the solution. By evaporating

the solution in iron, the cyanide of potassium is converted into ferro-cyanide of potassium and potash :—

3 at. KCy, 1 at. Fe, and 1 at. HO, form
1 at. 2 KCy + FeCy, 1 at. KO, and 1 at. H.

If the cream of tartar is mixed with a considerable quantity of saltpetre, and heated, the whole of the carbon becomes burnt, and instead of being black or gray, the deflagrated mass is white. The tartaric acid from 3 at. of tartar abstracts from the nitric acid of 10 at. of saltpetre, 30 at. of oxygen, forming 12 at. of water and 24 at. of carbonic acid; 13 at. of the latter combine with the potash of the cream of tartar and nitre, whilst the remainder is evolved with the water and nitric oxide :—

3 at. $KO + C_4H_2O_5HO + C_4H_2O_5$, and 10 at. $KO + NO_5$, form
13 at. $KO + CO_2$, 11 at. (free) CO_2, 15 at. HO, and 10 at. NO_2.

7056 Parts of cream of tartar require 12650 parts of nitre, or 1 part of cream of tartar $1\frac{3}{4}$ parts of nitre. I have already shown that in order to insure the entire combustion of the charcoal, an excess of nitre must be used, and thus the product is contaminated with nitrate of potash.

(*c.*) On saturating carbonate of potash with acetic acid, the carbonic acid is given off, and any silica present separates as a flocculent matter. From the solution acetate of baryta entirely precipitates the sulphuric acid, and acetate of silver the chlorides; the solution separated from the precipitate now contains acetate of potash, and any excess of the acetates of baryta or silver. On heating the dry saline mass to redness, the acetates of potash and baryta form carbonates, and the acetate of silver metallic silver; the last two products form with the carbon a residue, whilst the other products of decomposition of the acetic acid are given off. Nitrate

of baryta and silver must not be used instead of the acetates of these metals, as any excess of them would, on heating the salt to redness, cause the formation of cyanides. The whole of the salt must not be put at one time into the crucible, on account of the violence with which it froths up, but should be thrown in by spoonfuls.

Properties.—The pure carbonate of potash forms a snow-white crystalline odourless powder, of pungent caustic taste. In the air it attracts moisture, and deliquesces. At a white heat it fuses without change. It dissolves in water with the greatest readiness, forming a colourless solution; in alcohol it is insoluble. If the solution when diluted appears turbid, silica will be the principal cause of it, and caustic potash will almost entirely dissolve it.

Iron, carbonate of lime and *alumina*, in very small proportions, may be the cause of the turbidity. *Silica* may be present even if the salt is entirely soluble in water; in this case, test as directed under Kalium Oxidatum; to the same article I refer for the detection of *sulphuric acid*, *hydrochloric acid*, *alumina*, *magnesia*, *iron*, *copper*, and *lime*. *Cyanogen*, which is formed on heating common tartar, and also by deflagrating with nitre, may be detected by adding a somewhat oxidized solution of protosulphate of iron and then hydrochloric acid in excess, when if cyanogen is present Prussian blue will be formed. The chemical process is as follows: the cyanide of potassium, on evaporation in contact with iron, is converted into ferrocyanide of potassium, (and potassa), with which peroxide of iron in solution becomes decomposed into Prussian blue and a new salt of potash; for instance:—

3 at. $(2KCy + FeCy)$ and 2 at. $Fe_2O_3 + 3SO_3$, form
1 at. $3FeCy + 2Fe_2Cy_3$ and 6 at. $KO + SO_3$.

The blue precipitate is not visible until the car-

bonate of potash is saturated. Solutions containing protosalt of iron really give only a white precipitate of protocyanide of iron, but this precipitate quickly becomes blue :—

1 at. $2KCy + FeCy$ and 2 at. $FeO + SO_3$, form
3 at. FeCy and 2 at. $KO + SO_3$.

Manganese is rather frequently found in the potashes, imparting to them a slight bluish-green colour, but in such small quantities as scarcely to be evident to reagents. To detect *oxide of chrome*, which is almost always present, a peculiar process is employed ; the solution is agitated for several days with freshly precipitated carbonate of silver, the gray precipitate is collected and treated with very dilute nitric acid ; that part of the blackish-gray residue which is unacted on by the nitric acid, is heated to redness with carbonate of soda, the mass dissolved in boiling water, filtered, and the yellow filtrate supersaturated with hydrochloric acid, boiled, treated with caustic potash whilst warm, the precipitate dried and heated to redness. If the carbonate of potash was prepared from cream of tartar, carbonate of silver precipitates from it peroxide of iron, lime, silica, chlorine, and peroxide of chrome. The dark colour of the solution is due to organic compounds of silver, which arise from the action of filtering paper, dust, &c. The dilute nitric acid removes the excess of carbonate of silver with any traces of iron and lime. On heating the residue with soda, the oxide of chrome, at the expense of the oxygen of the atmosphere, is converted into chromic acid, which combines with a portion of the soda, another part of the soda forms with the silica present silicate of soda, and a third portion with the chloride of silver yields chloride of sodium and metallic silver. From the heated mass, water abstracts chromate of soda, silicate of soda and chloride of sodium. On supersaturating with hydrochloric acid, the silica pre-

cipitates; the filtered liquid acquires at the boiling temperature a green colour, the chromic acid causing evolution of chlorine and forming oxide or rather chloride of chrome:—

2 at. $NaO + CrO_3$ and 8 at. HCl, form
2 at. NaCl, 1 at. Cr_2Cl_3, 3 at. Cl, and 8 at. HO.

From this solution, caustic solution of potash precipitates oxide of chromium. The detection of the chromium in carbonate of potash is only of scientific interest, as at least half a pound of salt is requisite to obtain a satisfactory indication of it; the same process however serves to detect the lime, peroxide of iron, and silica, from which according to my experiments no carbonate of potash is absolutely free.* Attention has lately been called to carbonate of potash containing *carbonate of soda*; this may be partly accidental and partly intentional. To detect the admixture, the alkali is saturated exactly with acetic acid, warmed to drive off the carbonic acid, concentrated if necessary, and a solution of neutral antimoniate of potash added. If soda is present, a white granular precipitate of antimoniate of soda is formed, whilst pure acetate of potash will not be affected by it.

In order to determine the value of commercial potashes quickly, that is, the quantity of pure carbonate of potash they contain, the following method will be found simple and convenient. 100 Parts are dissolved in three times their weight of boiling

* I once received a sample of potashes containing so much iron in a soluble state that it could not be entirely freed from it, and was therefore converted into sulphate of potash. The iron was present as protoxide; exposed to the air it gradually acquired a yellowish brown colour, and on solution it gave a large residue of hydrated oxide of iron. On evaporating this solution to dryness, a pale greenish yellow salt was obtained, which also became of yellowish brown colour in the air. Sulphuret of potassium only caused the precipitation of a portion of the iron. These potashes contained neither nitric acid, nor cyanogen compounds. The whole appearances are in fact very striking and remarkable.

water, the solution filtered into a capacious porcelain dish, the contents of the filter well washed, and the filtered liquid after adding to it one or two drops of tincture of litmus is gently boiled, and a solution of 108 grains of pure tartaric acid in 392 grains of water added, so long as the liquid retains its blue violet colour. The excess of tartaric acid solution is then weighed, and the quantity used, being thus discovered, is divided by 5, the quotient giving the per-centage of pure carbonate of potash in the potashes. For instance, we take 500 grains of tartaric acid solution, of this 400 grains are requisite, consequently the potash contains $400 \div 5 = 80$ per ct. carbonate of potash. The tincture of litmus is employed to determine the point of saturation.

KALIUM OXIDATUM BICARBONICUM.

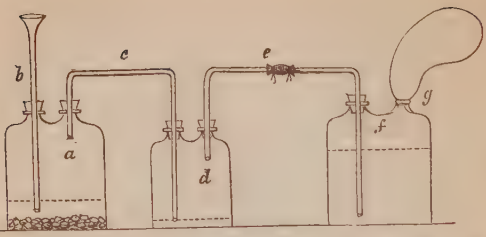
Potassæ Bicarbonas.—Bicarbonate of Potash.

FORMULA : $(KO + CO_2) + (HO + CO_2)$.

Preparation.—(*a.*) *With free carbonic acid.* A cheap and easy method of forming this salt is to place very shallow porcelain dishes in a wine or beer cellar, close to barrels, the contents of which are undergoing fermentation; the dishes are covered with purified potashes, to the depth of $\frac{1}{3}$rd of an inch, and then sufficient water added to moisten without liquifying it; every few days the mass is stirred, and in about a fortnight tested by diluting with water, filtering, and adding sulphate of magnesia to the solution. Should this cause a turbidness the potash must again be exposed to the atmosphere of carbonic acid, but if it remains unaffected the vessel is emptied into a tared porcelain evaporating dish, distilled water added to double the weight of carbonate of potash, and the dish warmed in a water bath. The temperature of the latter must never ex-

ceed 140° Fah., to insure which, a thermometer should always be kept in the water. When the salt has entirely dissolved, it is quickly filtered and the solution allowed to remain quietly some days in a cool place. The crystals which form are separated from the mother liquor, the latter evaporated to half, in a water bath, again allowed to crystallize, and the evaporation repeated. The mother liquor which now remains, is evaporated to dryness and used as simple carbonate of potash; the crystals are spread on filtering paper and exposed to the air in a cool dry place. They should weigh as much or rather more than the carbonate of potash used.

If obliged to prepare the carbonic acid purposely, the following process should be followed; in a double-necked bottle (a Woulff's bottle) are placed 1 part of carbonate of potash and 3 of water; in a second Woulff's bottle is put 1 part of carbonate of lime in small solid lumps, (marble or calcareous spar,) and 1 part of water; into one neck of this last bottle is fitted, by means of a cork, a long necked funnel, which reaches nearly to the bottom, and in the second neck a double-limbed tube, the other end of which fitting into the neck of a smaller Woulff's bottle just dips below the surface of the water which covers the bottom of the bottle, about an inch deep; this small bottle is also connected by a rather large double-limbed tube, with the first mentioned Woulff's bottle, and the end of the tube is placed a few inches deep into the solution of carbonate of potash. The first tube, connected with the bottle in which the gas is generated, may be of lead, the second must, however, be of glass, and is better cut in the middle and connected with a piece of caoutchouc to render it more moveable. The following woodcut will explain the arrangement better.



(*a*) is the generating flask containing the carbonate of lime, (*b*) the funnel tube, (*c*) the leaden tube, (*d*) the wash bottle, (*e*) the glass tube, (*f*) the bottle of potash solution. All openings excepting the tubulate (*g*) are carefully closed, and a portion of common hydrochloric acid, spec. grav. 1·130 is poured through the funnel (*b*); as soon as the effervescence ceases, a second portion of acid is added; the bottle (*b*) should be occasionally agitated. When the gas has been evolved about a quarter of an hour, a moist bladder, freed from air, is fastened to the tubulate (*g*). The bladder will be filled by the acid which escapes absorption in passing through the liquid, but as the stream slackens it again collapses. As more acid is added to the carbonate of lime the bladder again expands and re-collapses as before this continues until the alkaline solution is thoroughly saturated, when it remains filled, and the liquid rises in the funnel tube (*a*); this point is reached when the carbonate of lime is dissolved, and about 3 parts of acid have been used. As the operation must not be hurried, the evolution of gas is not aided by heat. From the absorption of carbonic acid the contents of the flask (*f*) gradually rise in temperature, this must not be lowered artificially, as the heat faciltates the formation of the bicarbonate of potash. If, after standing some hours,

the bladder becomes entirely collapsed, more carbonic acid must be evolved from (*a*), but this is seldom requisite. The contents of the flask (*f*) are now put into a porcelain dish, warmed and crystallized as before directed.

(*b.*) *With carbonate of ammonia.*—On the small scale bicarbonate of potash may be conveniently made by dissolving 2 parts of carbonate of potash with 6 parts of water in a porcelain dish, and adding 1 part of powdered carbonate of ammonia; the whole is warmed in a water-bath (see previous directions) until ammoniacal fumes are no longer evolved, then filtered, placed in a cool spot to allow the crystals to separate, and the mother liquor concentrated once or twice; the last portions of it may be evaporated to dryness, the residue being simple carbonate.

Recapitulation.—(*a.*) The simple carbonate of potash is capable of absorbing 1 entire atom of carbonic acid, and forming with it a readily crystallizable salt. Any silica the potash may contain will thus be separated and rendered insoluble. The carbonic acid which is obtained from alcoholic fermentation is formed by the separation of the sugar in the presence of a ferment into this gas and alcohol:—

1 at. $C_{12}H_{12}O_{12}$ (anhydrous grape sugar), forms
2 at. $C_4H_6O_2$ and 4 at. CO_2.

By moistening the salt, carbonic acid is more readily absorbed. The testing with sulphate of magnesia is to ascertain whether much simple carbonate of potash remains, in which case a precipitate of carbonate of magnesia will be formed, whilst the bicarbonate of potash, although decomposed, (it forms bicarbonate of magnesia and sulphate of potash,) is not rendered turbid (in the cold). This test answers the purpose, but it is not very accurate, as bicarbonate of potash containing only a small

quantity of carbonate gives no precipitate with sulphate of magnesia. On warming the salt with water to obtain a complete and saturated solution, the latter must not be raised higher than the given temperature, far less to the boiling point, otherwise the 1 atom of carbonic acid is given off, and the salt again reduced to the simple carbonate. The loss of a little carbonic acid is unavoidable, and we must not expect to obtain the whole of the carbonate employed, as bicarbonate; this is of no great consequence, as after the second or third crystallization the mother liquor is used as simple carbonate.

In using carbonate of lime and hydrochloric acid to generate carbonic acid, chloride of calcium and water are formed, and remain in the generating bottle:—

1 at. $CaO + CO_2$ and 1 at. HCl, form
1 at. CaCl, 1 at. HO and 1 at. CO_2.

625 Parts of carbonate of lime require 455 parts of anhydrous or 1750 parts of hydrochloric acid, spec. grav. 1·130 (containing 26 per ct.). The gas in escaping carries with it traces of chloride of calcium, and in order that the potash solution may not be contaminated, it is first conducted through the wash bottle *d*. In order that the evolution of gas may not be too violent, solid pieces of carbonate of lime are used. The hydrochloric acid cannot well be replaced by dilute sulphuric acid, as this forms on the carbonate of lime a crust of difficultly soluble gypsum, which prevents the further action of the acid. The carbonic acid evolved from 625 parts of carbonate of lime should be sufficient to convert 865 parts of carbonate into bicarbonate; for

1 at. CO_2, 1 at. $KO + CO_2$ and 1 at. HO, form
1 at. $(KO + CO_2) + (HO + CO_2)$.

Rather more than this proportion must be generated, and the quantity of carbonate of lime consequently

increased, in order to allow for that absorbed by the fluid of the two first bottles. The bladder fastened to the tubulus of the bottle *f* serves partly to prevent the escape of gas, and partly as an indicator of its point of saturation, from the excess of gas keeping it expanded. The bladder must not be fastened on, until the carbonic acid has expelled all the atmospheric air; if this precaution be not taken, the bladder will not only prevent the passage of the carbonic acid, but, remaining filled with atmospheric air, will be no guide as to its saturation. Another evil experienced by at once attaching the bladder is, that, from the pressure of the atmospheric air which is forced by the gas into the bottle *f*, the liquid is forced through the funnel tube, long before the operation is ended. The rest of the manipulation has been already explained.

If carbonate of potash from potashes is employed, the first gas passed through causes a precipitation of silicic acid, (which it displaces,) and after some little time, if the proportion of water is small, a separation of crystals of bicarbonate of potash occurs. A wide glass tube is employed to prevent its stoppage by the crystals. If the potash is not very impure the last of the mother liquor will contain the whole of the sulphate of potash, chloride of potassium, &c.

The liquid in the generating flask may be used for chloride of calcium.

(*b.*) In the warm, carbonate of ammonia gives up its acid to the carbonate of potash, forming bicarbonate, whilst ammonia is evolved. It is quite immaterial whether the sesquicarbonate or bicarbonate of ammonia is employed; for

3 at. $KO + CO_2$, 1 at. $2NH_4O + 3CO_2$, and 1 at. HO, form
3 at $(KO + CO_2) + (HO + CO_2)$ 2 at. NH_3;

or,

2 at. $KO + CO_2$ and 1 at. $(NH_4O + CO_2) + HO + CO_2$, form
2 at. $(KO + CO_2) + HO + CO_2$, and 1 at. NH_3.

2595 Parts of carbonate of potash require 1475 parts of sesquicarbonate of ammonia, or 1730 parts of the former 988 parts of the bicarbonate, being about 2 parts of carbonate of potash to 1 part of either of the ammoniacal salts. In this case, if the carbonate of potash contains silica, this is precipitated. It is scarcely possible to economize the ammonia evolved, as the fluid requires very frequent stirring.

Properties.—The bicarbonate of potash forms permanent, transparent, oblique, rhombic prisms, or tabular crystals; it is odourless, of a mild, saline (somewhat caustic) taste. Heated it loses, without fusing, half its carbonic acid and water, simple carbonate of potash remaining. Cold water dissolves one-fourth, hot water its own weight of the salt. The solution has a feebly alkaline reaction, which in the heat becomes alkaline, from the formation of simple carbonate. Alcohol only takes up traces of the salt. If it becomes moist when exposed to the air, it contains simple *carbonate of potash*, and sulphate of magnesia will cause a turbidness in the solution; but, as before stated, this test is not very accurate, small quantities of carbonate of potash in the bicarbonate escaping detection. A solution of bichloride of mercury answers the purpose better, causing with bicarbonate of potash a white precipitate of bicarbonate of peroxide of mercury, which, after a short time, liberates carbonic acid and remains as a brownish red basic carbonate; whilst if the salt contains simple carbonate the precipitate will from the first be of a yellow or brownish colour. Other impurities, as *sulphuric* or *hydrochloric acids* or *metals*, are to be looked for as directed under KALI CAUSTICUM.

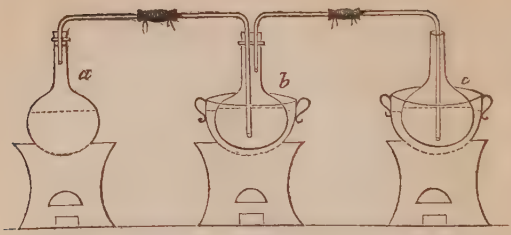
KALIUM OXIDATUM CHLORICUM.

Potassæ Chloras.—Chlorate of Potash.

FORMULA: $KO + ClO_5$.

Preparation.—3 Parts of carbonate of potash are dissolved in 20 parts of water, the same intimately rubbed with 8 parts of caustic hydrated lime to a uniform creamy consistence, and the mixture put into a flask, which it must not more than ¾ fill. The flask is closed with a cork in which two holes are bored, one of these is to admit the glass tube, through which the chlorine is conducted, and must reach nearly to the bottom, the second contains a double-limbed tube which passes nearly to the bottom of a second flask, also containing a mixture of 3 parts of carbonate of potash, 20 parts water and 8 parts hydrate of lime. The tubes must not be less than ¼ of an inch in diameter, and the two limbs should be separate and connected with caoutchouc to render them more moveable, and less liable to breakage. Both flasks are placed with straw beneath them in a water bath. The chlorine gas is evolved from a mixture of 1 part peroxide of manganese, 1 part of water, and 3 parts of common hydrochloric acid, spec. grav. 1·130. The annexed drawing explains the apparatus.

All openings are carefully closed with luting and bladder, excepting the mouth of the flask (*c.*), which is only loosely covered with bladder. As soon as the chlorine begins to be evolved, which must be assisted by applying heat to the generating flask) the water baths containing (*b*) and (*c*) are brought nearly to the boiling point; as the process goes on, this artificial heat is unnecessary, the absorption of the chlorine raising the temperature sufficiently. The flasks must every now and then



be agitated. The chlorine is continued until the contents of the flask (*b*) have become entirely or nearly clear, and for this, with 3 parts of carbonate of potash, and 8 of hydrate of lime, in each flask, 50 parts of peroxide of manganese, and 150 of muriatic acid must be used. The apparatus, to prevent absorption, is separated before it cools, the flask (*b*) removed, (*c*) put in its place, another flask filled with a similar mixture of carbonate of potash, lime, and water, substituted for (*c*), the stream of chlorine continued until the contents of (*c*) are saturated, and so continued until sufficient chlorate of potash has been obtained. The number of flasks saturated does not affect the process; (*c*), or that which has not sufficient gas through it, is set on one side; (*b*) is heated in a water bath until it gives off no more smell of chlorine, its contents then diluted with sufficient water to make it weigh 36 parts, and again heated and filtered as soon as all the salt is dissolved. The liquid is put in a cool spot, the crystals, which separate, are after some days removed from the mother liquor and the latter again evaporated to crystallization. If, after so treating it two or three times, the mass solidifies, a little cold water is added, which readily dissolves the chloride of calcium, but leaves most of the chlorate of potash. The salt is then collected and purified by

recrystallization. The produce from 3 parts of carbonate of potash, and 8 of hydrate of lime, should be from 4 to $4\frac{1}{2}$ parts.

Should it be desirable to use chloride of potassium, which frequently occurs in chemical processes as a secondary product, this is substituted for carbonate of potash, the proportions being 3 parts of chloride of potassium, 20 parts of water, and 9 parts of hydrate of lime. It is perhaps advantageous even to neutralize the carbonate of potash with common hydrochloric acid, if we have no chloride of potassium, and use the solution (taking into calculation the water it contains).

Recapitulation.—When chlorine is passed into dry hydrate of lime, or milk of lime, it forms in the first instance a bleaching compound (chloride of lime); the oxygen of 1 at. of lime uniting with 1 at. of chlorine to form hypochlorous acid, which combined with 1 at. of lime forms hypochlorite of lime, the important bleaching principle of chloride of lime. A second atom of chlorine combines with the reduced atom of calcium to form chloride of calcium:—

2 at. CaO, and 2 at. Cl, form
1 at. CaO + ClO, and 1 at. CaCl.

A large portion of the lime remains still unchanged, and the mixtnre forms the chloride of lime of commerce. If more chlorine is passed into this mixture, the free lime is converted into the bleaching compound, but, at the same time, that already formed experiences a second change, to which finally, if sufficient chlorine is employed, the whole of the lime is subject. The chloride of calcium formed remains unaltered, but the hypochlorite of lime is so decomposed that 3 parts of it form 2 at. chloride of calcium, and 1 at. chlorate of lime:—

3 at. CaO + ClO, form
2 at. CaCl, and 1 at. CaO + ClO_5.

so that the final result from 6 at. lime, and 6 at. chlorine, are 5 at. chloride calcium, and 1 at. chlorate lime :—

6 at. CaO, and 6 at. Cl, form
5 at. $CaCl_2$, and 1 at. $CaO + ClO_5$.

Potash (or soda) behaves like lime, and if 1 at. of lime is replaced by 1 at. of potash, an atom of chlorate of potash is formed, by reason of its more difficult solubility than chlorate of lime, and no chloride of potassium. If, instead of pure potash, we employ carbonate of potash, carbonate of lime becomes formed, but this is afterwards changed into chloride of calcium, the carbonic acid being given off. Formerly only potash was employed in the preparation of this salt, but as $\frac{5}{6}$ of the potash went to form chloride of potassium, a salt of but little value, the cost was very much enhanced; by employing lime to afford oxygen to the chlorine, the cost is lessened, but the cheapest method is, to substitute for the carbonate of potash, chloride of potassium, which is often obtained as a secondary or waste product (as in the preparation of tartaric acid (*a*)); for 1 at. of this 6 at. of lime are requisite; for,

1 at. KCl, and 6 at. CaO, form
6 at. CaCl, and 1 at. $KO + ClO_5$.

2775 Parts of hydrate of lime require 933 parts of chloride of potassium, or 5 at. = 2312 parts of hydrate of lime, 865 parts of carbonate of potash. In order to convert the potash into chlorate, and the lime into chloride of calcium, 6 at. = 2658 parts of chlorine are necessary, and these are equivalent to 2733 parts of anhydrous hydrochloric acid, or 10500 parts of acid, spec. grav. 1·130. Under the article Chlorum Aquosum, it is shown that on treating peroxide of manganese with hydrochloric acid, the chlorine of only half the latter is evolved,

the other half combining with the manganese, consequently the quantity of acid must be doubled. But practice shows that 21000 parts of hydrochloric acid are not sufficient to convert 1 at. potash and 5 at. lime into chlorate of potash and chloride of calcium, as a portion of chlorine always escapes uncombined, and cannot be prevented so doing; for this reason a much larger proportion of manganese and hydrochloric acid is ordered than would appear from calculation to be necessary. In order to prevent this chlorine from being lost, a second bottle (*e*) is attached; from this a little chlorine will also escape, but I cannot recommend that more flasks should be attached, as it would render the apparatus too unwieldy. At the commencement of the process the absorption of chlorine is so perfect, that not a trace of it can be detected close to the apparatus; when about half-finished the empty space in the flask (*b*) has a greenish-yellow appearance, and, from this period, gas continues to pass into the flask (*c*). The absorption of the chlorine is considerably facilitated by warming the alkaline mixture, if this is omitted at least as much more chlorine is requisite, and both time and material are wasted. Not more than 24 parts of water must be employed with 8 parts of lime, as the more concentrated the solution the more quickly is the chlorine absorbed. In order that the glass tube may not become stopped up, either by the thick pasty mass or the salt which forms, one at least $\frac{1}{3}$ of an inch in diameter should be employed. When the chlorine has been passed into it for some little time, the mixture acquires a rose colour, from the formation of ferric acid; oxide of iron is a never-failing contamination of lime:—

1 at. Fe_2O_3, 3 at. Cl, and 3 at. HO, form
2 at. FeO_3, and 3 at. HCl.

Gradually the milk of lime becomes thiner, until

(with the above quantities of manganese and acid) it almost entirely disappears, and is replaced by a part of the chlorate of potash formed, which crystallizes on cooling. The warming in an uncovered flask is to remove the excess of chlorine, and decompose the ferrate of potash which separates, into free potash, peroxide of iron and oxygen :—

2 at. $KO + FeO_3$, yield
2 at. KO. 1 at. Fe_2O_3, and 3 at. O.

The mother liquor from the chlorate of potash crystals can, when dried and heated to redness, be used as common chloride of calcium.

Properties.—Pure chlorate of potash forms permanent transparent mother-of-pearl like, oblique rhombic plates, which are odourless and possess a cooling disagreeable taste. Heated it fuses, and evolves oxygen, becoming finally converted into chloride of potassium :—

1 at. $KO + ClO_5$, forms
1 at. KCl, and 6 at. O.

The details of this decomposition are given under the article KALIUM SUPERCHLORICUM. With combustible substances as carbon and sulphur it gives, when triturated, a detonation which even with small quantities is highly dangerous : the oxygen in this salt not being very firmly united, separates from it even at the ordinary temperature, when it has the opportunity of combining with other substances. With sulphur it forms sulphuric acid, which unites to the potash, and chlorine with the excess of oxygen is given off :—

1 at. $KO + ClO_5$, and 1 at. S, form
1 at. $KO + SO_3$, 1 at. Cl, and 2 at. O.

With carbon, there are produced carbonic acid, which is given off, and chloride of potassium remaining :—

1 at. $KO + ClO_5$, and 3 at. C, form
1 at. KCl, and 3 at. CO_2.

The detonation is caused by the oxygen which is liberated driving away the atmospheric air, but being again instantly condensed, (*i.e.* combining with the combustible body,) the latter rushes back into its former place. At the ordinary temperature, the salt dissolves in 16 parts, at the boiling temperature in 2 parts of water : alcohol of 80 per ct. dissolves only $\frac{1}{120}$ at the common temperature, but much more when boiling. The solution has neither an acid nor an alkaline reaction. This salt is generally contaminated with *chloride of potassium ;* in which case nitrate of silver causes the well-known precipitate of chloride of silver. If it attracts moisture from the air, it is not free from *chloride of calcium*, which is to be detected by oxalate of ammonia. A yellow colour indicates *iron* which is proved by ferrocyanide of potassium. The admixture of *nitrate of potash* with it is known on heating a portion for some time to redness, by its solution imparting a brown colour to turmeric paper. The saltpetre when heated loses a portion of its acid, (*vide* KALI NITRICUM,) whilst chlorate of potash when heated gives only neutral chloride of potassium.

KALIUM OXIDATUM NITRICUM DEPURATUM.

Potassæ Nitras.—Purified Nitrate of Potash.—Purified Saltpetre.

FORMULA : $KO + NO_5$.

Preparation.—Previously to purifying the common nitre of commerce, it is tested for lime and magnesia ; if oxalate of ammonia renders the solution turbid, the former of these is present ; and on

separating this precipitate, a second one caused by phosphate of ammonia indicates the latter. If this be the case, the nitre is dissolved in 5 times its weight of pure water, and for every pound of salt ¼oz. of hydrate of lime is added, the whole well stirred is allowed to stand for some days and then filtered. To the clear liquid, a solution of carbonate of potash is added by drops, so long as it causes a precipitate, and again filtered. The filtrate is now evaporated in a clean copper vessel until it is reduced to about 1⅓ times the weight of the saltpetre used, then poured into an earthenware or porcelain dish, and stirred with a porcelain or wooden spatula until cool; the cooling may be assisted by placing the dish in cold water, ice, or snow. The granulated saltpetre thus obtained is, together with the supernatant mother liquor, put into a percolator, varying in size according to the quantity of the salt. When the mother liquor has drained off as much as possible, pure cold water is poured on the top, until the solution which escapes no longer becomes turbid when tested with nitrate of baryta; when this point is attained, a cold saturated solution of chemically pure nitre is added in the same manner, until nitrate of silver solution no long causes a precipitate in it; if chemically pure nitre is not to be obtained, cold water must be substituted, but this causes a great waste of salt. The saline mass thus purified is spread upon linen and dried with a gentle heat; the yield will be ⅔ to ¾ of the raw material employed.

The mother liquors, wash waters, &c., are collected and evaporated, either to a second crystallization, or else to dryness, and used in processes where a little colouring matter, chloride of potassium, or sulphate of potash is unimportant; as *antimonium diaphoreticum*, &c.

It is of course understood that when neither lime nor magnesia is present, the treatment with lime

and carbonate of potash may be omitted. The salt is then only dissolved in twice its weight of boiling water, filtered whilst hot, the clear solution evaporated to $1\frac{1}{2}$ times the weight of the original substance and granulated as in the first case.

Recapitulation.—Common saltpetre generally contains, besides extractive (colouring) matter, small portions of lime and magnesian salts, whilst chlorides and sulphates as well as soda salts are always present. The lime and magnesian salts might be removed in the same manner as other impurities, but then these would remain in the mother liquor and render it inapplicable in cases where sulphates, chlorides, soda salts, and colouring matter were not detrimental. For this reason the lime and magnesia must be entirely removed. The lime which is added being a more powerful base displaces and precipitates the magnesia, increasing of course the quantity of lime salt, but which is in its turn thrown down by carbonate of potash, as insoluble carbonate of lime. The liquor so far purified is not evaporated to crystallization, as the crystals will retain enclosed within them a certain portion of mother liquor which renders them impure, and it is on this account that all large crystals of nitre adhere together when powdered, and appear moist. The liquor is therefore evaporated as much as possible, and then well stirred to destroy the crystals as they form. The evaporation may be carried on in clean copper, but the granulation (destroying the crystals) must be performed in a porcelain dish, as the metal is readily attacked by the salt in the cold. The granulation of course proceeds most rapidly and perfectly in the winter, when ice or snow may be obtained as cooling agents. By washing with cold water (which is also better performed in winter) the colouring matter and any soda salts are next removed and then the sulphate of potash and chloride of potassium, which also carry with them some of

the nitre in solution. If we used only water to free the nitre from all chloride of potassium, a large quantity of nitrate of potash would be washed away before the liquid ceased to cause a turbidity with nitrate of silver. For this reason whenever it is practicable, a concentrated solution of pure nitrate of potash is employed, for as this solution penetrates the mass it takes up the more readily soluble chloride of potassium, leaving in its place an equivalent quantity of nitrate of potash; in this case also a slight loss of weight is experienced, for a given quantity of water dissolves in the cold more chloride of potassium than nitrate of potash.

Properties.—Pure nitre appears as a snow-white crystalline powder, odourless, and of a cooling bitter saline taste. Heated it fuses to a colourless liquid, but, if allowed to continue long in this state, it gives off oxygen, and becomes converted into nitrite of potash ($KO + NO_3$), afterwards this also is decomposed, oxygen and nitric oxide are given off, and pure potash remains. A long-continued red heat is, however, necessary to entirely decompose even a small quantity of nitrate of potash. It dissolves in 4—4½ parts of water of the ordinary temperature, but requires only the half its weight of boiling water; the solution has a neutral reaction, and forms by slow evaporation anhydrous fluted prisms of a considerable size, which belong to the right rhombic system. These crystals, as before stated, having some of the mother liquor enclosed, yield a moist powder. If on exposure to the air the nitre becomes moist it contains some deliquescent salt, most likely of *lime* or *magnesia*. In either case carbonate of potash will cause a turbidity; but the lime is more accurately detected by oxalate of ammonia, and, after the precipitation of the oxalate of lime, the magnesia by phosphate of ammonia (*vide* AMMON. CHLORATUM DEPURATUM.). *Soda* is determined in the concentrated mother

liquid by antimoniate of potash; (*vide* KALI CARBON.); *sulphuric acid* by a baryta salt, and *hydrochloric acid* by a salt of silver; *copper* from its chocolate-coloured precipitate with ferrocyanide of potassium, and *iron* from its blood-red solution with sulphocyanide of potassium. (*Vide* ACID. ACET. and and BISMUTH NITR.)

To form the nitrum tabulatum (sal prunella), some ounces are fused in an iron spoon, which has, in its side, about one quarter of an inch from its edge, a small hole bored about the size of a pin's head, through which the fused mass is allowed to pour on to a clean sheet of iron or copper, and so on with fresh quantities of salt. When subsequently fusing, care must be taken that none of the fused salt adheres to the outside of the spoon, as on coming in contact with the coal it will deflagrate and form carbonate; for the same reason no coal must be allowed to fall into the spoon. Excepting a small quantity of nitrite of potash which is formed during the fusion, the fused nitrate of potash exactly resembles in its chemical constitution the ordinary saltpetre.

KALIUM OXIDATUM OXALICUM NEUTRALE.

Potassæ Oxalas.—Neutral Oxalate of Potash.

FORMULA: $KO + C_2O_3 + 3HO$.

Preparation.—8 Parts of binoxalate of potash are warmed in a capacious porcelain dish with 30 parts of pure water, and pure carbonate of potash gradually added so long as it causes an effervescence; the liquid is tested with litmus and turmeric; it should have a neutral reaction. For this end from 5—6 parts of carbonate of potash are required.

The solution is filtered and allowed to crystallize. The produce will be 11 to 12 parts.

Recapitulation.—In order to convert the binoxalate of potash $= (KO + C_2O_3) + (HO + C_2O_3) + 2HO$ into the neutral salt 1 at. of carbonate of potash is required; or for 1828 parts of binoxalate, 865 parts of carbonate of potash. As, however, the commercial binoxalate almost always contains quodroxalate, which, instead of 49 contains 56 per ct. oxalic acid, 1 at. of carbonate of potash is not, generally speaking, found to be sufficient to neutralize the acid reaction. It is not necessary to dissolve the binoxalate of potash in water, for in becoming neutral it acquires a greater solubility.

Properties.—Neutral oxalate of potash forms permanent colourless prismatic crystals, which are odourless, with a bitter cooling taste. Heated it fuses, first giving off its water, and then the oxalic acid entirely decomposes into carbonic oxide and carbonic acid:—

1 at. C_2O_3, forms 1 at. CO_3 and 1 at. CO.

The carbonic oxide is given off, but the carbonic acid remains in combination with the potash. Cold water dissolves half its weight of this salt, hot water considerably more; in alcohol it is insoluble. The aqueous solution has at first a neutral reaction, but on keeping for some time becomes alkaline, carbonate of potash being formed (the decomposition is exactly similar to that it undergoes at a red heat); and of course it now effervesces with acids. In testing for impurities those substances most likely to be found in carbonate of potash must be looked for, as *iron*, *alumina*, *magnesia*, *hydrochloric acid*, and *sulphuric acid*. The most probable adulterations are *nitre*, *sulphate*, or *bitartrate of potash*. The nitre is detected by the salt deflagrating when heated to redness on charcoal; the aqueous solution containing sulphate of potash gives a precipitate

with chloride of barium insoluble in hydrochloric acid: bitartrate of potash is known by the peculiar odour it evolves when burnt, and the black carbonaceous residue it leaves.

KALIUM OXIDATUM SILICICUM SOLUBILE.

Soluble Silicate of Potash.—Soluble Glass.

FORMULA: $KO + 2SiO_2 + xHO$.

Preparation.—(a) With cream of tartar.—2 Parts of finely-powdered rough tartar are intimately mixed with 1 part of finely-powdered quartz (or silver sand), the mixture pressed into an earthen crucible, which it must only ⅔ fill, the crucible placed on a brick in a good wind furnace, covered with a tile, and slowly heated to redness. The heat must be continued until neither smoke nor flame escapes from the crucible, and the contents no longer froth up, but quietly fuse. The syrupy mass is now poured into an iron pot; when cold it is powdered, and, together with the crucible, to which a good portion always adheres, is exhausted by boiling with 12 parts of water; when all has dissolved, the crucible is removed and the solution filtered hot. The clear solution is evaporated until a portion taken from it acquires, on cooling, a gelatinous consistence; it is then poured into a glazed dish, and kept in a cool place. Nearly 2 parts of gelatinous soluble glass are obtained.

(b) With carbonate of potash.—For technical purposes, where large quantities are of more consideration than an absolutely pure product, common potashes may be used to replace the cream of tartar. 10 Parts of common potash, 12 parts of finely-powdered quartz, and 1 part of charcoal powder, are

intimately mixed, and heated in a crucible until they become quietly liquified; the mass is then poured out, and boiled in an iron pot with 100 parts of water, the solution placed in an earthen vessel, a small portion of finely-powdered carbonate of lead added, and well agitated with it. If a filtered portion imparts to lead paper (paper saturated with a solution of acetate of lead) no brown or black colour, it shows that all the sulphuret of potassium formed during the fusion is decomposed; if otherwise, small portions of carbonate of lead are gradually added until the lead paper is no longer acted on. The solution thus purified is filtered and evaporated to the same consistence as under (*a*). The product will weigh about as much as the material employed.

Recapitulation.—It has been already explained, under the article "KALIUM," that when cream of tartar is burnt the acid is decomposed, and the residue consists of carbonate of potash and carbon. At a red heat silicic acid combines with the base of the carbonate, driving off its acid; this reaction takes place only by a long-continued and powerful heat, but is greatly assisted when the carbonic acid is capable of forming carbonic oxide gas. For this purpose, the finely-divided charcoal remaining intimately mixed in the heated mass is of the greatest advantage, and far more efficacious than when carbonate of potash, quartz, and charcoal powder are mixed artificially:—

1 at. $KO + CO_2$, 2 at. SiO_3, and 1 at. C, form
1 at. $KO + 2SiO_3$, and 2 at. CO.

865 Parts of carbonate of potash require 1154 parts of silicic acid, and 75 parts of carbon, if the materials are pure; but as such would be too expensive, a slight excess of potashes and charcoal is ordered, to allow for the impurities which they contain, whilst these in silver sand seldom exceed 1

per ct. Instead of purified cream of tartar, the common may be used; as 1 at. cream of tartar, $= \dot{K}O + \overline{T}_2 + \dot{H}O + \overline{T}_2$ forms 1 at. carbonate of potash, so 1154 parts of silicic acid are requisite for 2352 parts of cream of tartar. The bitartrate of lime, with which the common cream of tartar is always contaminated, becomes at the same time converted into silicate of lime, which, on treating the fused mass with water, remains behind. The common tartar is never free from sulphate of potash, and from the reduction of this by the carbon, the fused mass always contains sulphuret of potassium:—

1 at. $KO + SO_2$, and 4 at. C, form
1 at. KO, and 4 at. CO.

This sulphuret of potassium, which imparts to the preparation a disagreeable hepatic taste, is readily removed by agitating with carbonate of lead, carbonate of potash and insoluble sulphuret of lead being formed. The evaporation of the solution only to a jelly is better than continuing it to dryness, as in the latter case it is less soluble in water.

Properties.—Soluble glass thus prepared is a yellowish-brown transparent mass, breaking between the fingers, but quickly again uniting to form a jelly, of a strongly alkaline taste and reaction. When warmed, it first becomes liquid, and finally dry. Heated to redness it again fuses, forming when cold a clear hard glass, which does not become moist, but gradually loses its transparency in the air. The gelatinous compound readily dissolves in warm water, whilst the dried requires a continued boiling. Acids coagulate the solution, by combining with the potash and precipitating the silicic acid. If, at the same time, an effervescence is caused, the preparation is not free from *carbonate of potash*; whilst, under the same circumstances,

an odour of sulphuretted hydrogen indicates *sulphurets*. Imperfect solubility in water is probably due to *lime*, *iron*, &c.

KALIUM OXIDATUM STIBICUM ACIDUM.

Potassæ Bi-Antimonias.—Antimonium Diaphoreticum Ablutum of some Pharmacopœias.—Bin-Antimoniate of Potash.

FORMULA: $KO + 2Sb_2O_3 + 6HO$.

Preparation.—4 Parts of powdered metallic antimony are intimately mixed with 10 parts of nitrate of potash, and $\frac{1}{4}$ part of powdered charcoal, and thrown, a spoonful at a time, into a red-hot Hessian crucible. When all deflagration has ceased, the mass is heated for $\frac{1}{2}$ an hour, the crucible allowed to cool, its contents removed and powdered, then thrown into cold water, well stirred with a wooden spatula for some hours, and allowed to subside, (the crucible is also inverted in a vessel of water until the portions adhering to it have detached themselves, and may then be mixed with the bulk). When the solution is quite clear it is poured off, fresh water is added to the residue, and this washing repeated so long as the alkaline reaction is retained. The white residue is collected on a strainer, and dried with a gentle heat. It should weigh from 5 to $5\frac{1}{2}$ parts.

In making this preparation, the sulphuret of antimony is generally substituted for the pure metal; 4 parts of the sulphuret require 12 parts of nitre, and no charcoal. Thus prepared, the Antimon. Diaphor. is generally contaminated with iron or lead, and has a yellow colour. The yield is nearly the weight of the sulphuret of antimony used.

Recapitulation.—For an explanation of the de-

flagration, I must refer to the process under the article ACID. STIBICUM. The mass, which consists of antimoniate and nitrite of potash, on being treated with water is separated, the nitrite of potash dissolves, and the antimoniate of potash decomposes into an acid salt, which precipitates, and free potash, which, dissolving again, takes up a portion of the acid salt :—

$$2 \text{ at. } KO + Sb_2O_5, \text{ form}$$
$$1 \text{ at. } KO + 2Sb_2O_5, \text{ and } 1 \text{ at. } KO.$$

For this reason a portion of the antimoniate of potash is lost on washing, and if boiling water is used the loss is still more considerable.

By using sulphuret of antimony instead of the pure metal, the sulphur becomes oxidized to sulphuric acid, so that in this case the deflagrated mass contains, besides antimoniate and nitrite, also sulphate of potash :—

$$1 \text{ at. } Sb_2S_3, \text{ and } 5 \text{ at. } KO + NO_5, \text{ form}$$
$$1 \text{ at. } KO + Sb_2O_5, 3 \text{ at. } KO + SO_3,$$
$$1 \text{ at. } KO + NO_5, \text{ and } 4 \text{ at. } NO_2.$$

2212 Parts of sulphuret of antimony require 6325 parts of nitre ; or, 3 parts of the latter to 1 of the former. The addition of charcoal is unnecessary, as the sulphuret of antimony alone gives with the nitre a lively deflagration.

Water has a similar action in this case : it abstracts the sulphate, nitrite, free potash, and a little antimoniate of potash from the mass, leaving the acid antimoniate of potash behind.

Properties.—Acid antimoniate of potash is a white, odourless, and tasteless powder. To determine the potash it contains, digest with dilute nitric acid, filter, evaporate to dryness, and weigh the nitre formed. Prepared with sulphuret of antimony it generally has a yellow colour, arising from *oxide of iron* or *lead ;* these bases, as well as oxide

of antimony, may be detected by the process given under the article ACID. STIBICUM.

KALIUM OXIDATUM STIBICUM NEUTRALE.

Potassæ Antimonias Neutralis.—Neutral Antimoniate of Potash.

FORMULA: $KO + Sb_2O_5 + 7HO$.

Preparation.—4 Parts of metallic antimony, 10 parts of nitrate of potash, and ¼ part of charcoal are deflagrated by the process just given; the mass thus obtained is rubbed up with ten times its weight of cold water, the turbid liquid allowed to subside in a glass cylinder, and the supernatant liquid poured off as thoroughly as possible; the residue is now placed in a narrow-necked flask, sufficient water added to bring the weight up to twenty times that of the deflagrated mass, and heated to boiling. After boiling some hours, the water which has evaporated is replaced, and the whole filtered; to the filtered solution sufficient caustic potash solution is added to give it a strong alkaline reaction, and then evaporated so far that the residue weighs scarcely as much again as the deflagrated mass. After standing some days, this residual liquid becomes entirely or partially converted, in the cold, into a transparent, soft, resinous like substance; any supernatant liquid is decanted, the mass itself mixed with three times its volume of cold water, and agitated until it is converted into a granular powder, then thrown on a filter and dried. The liquid which separates from this is evaporated, the residue treated with cold water, and obtained as a fine granular powder. The liquid remaining gives, on evaporation and treatment with cold water, still more of the granular salt; of

which altogether the yield will be half the weight of the regulus of antimony used.

Recapitulation.—As regards the deflagration, I must refer to the article ACIDUM STIBICUM. By the first washing with water, the nitrite of potash, which in a further stage of the process would exert an injurious influence, is mostly removed, whilst the residue (antimoniate of potash) is only partially converted into the acid salt (*vide* the previous article). By continuous boiling with water the neutral antimoniate of potash is abstracted, and the antimonic acid, formed by the separation of the neutral from the acid salt, remains undissolved. To this antimonic acid traces of potash always adhere, as well as the impurities of the antimony, iron, copper, lead, &c., as antimoniates of the oxides of these metals. The filtered solution might be at once evaporated, without the addition of potash, in order to obtain the granular antimoniate of potash, but this salt on crystallizing fixes itself so firmly to the sides of the dish, that it can only be partially removed. It is therefore most advantageous to make the solution strongly alkaline, previous to evaporating, by which the crystallization of the granular salt is prevented, and the gummy salt $= KO + Sb_2O_5 + 5HO$ (the above mentioned soft resinous mass) formed. On treating this gummy salt with cold water, it is mostly converted, by taking up 2 at. of water, into the difficultly soluble granular salt, whilst a small portion together with the free potash remain in solution. By evaporating this solution and treating with cold water a further portion of the granular salt is obtained.

Properties.—The granular antimoniate of potash is a snow-white, fine tasteless powder. On heating it loses its water without undergoing a further visible change. In water it is but difficultly soluble, requiring 250 of cold and 90 parts of boiling water for its solution; these solutions have a

neutral reaction. In spite of its difficult solubility, this salt is very valuable as a test for soda, for the cold saturated aqueous solution (made by digesting 2 grains of salt with an ounce of water and filtering) gives in solutions of soda salts, if not too dilute, at once, or after a short time, a fine granular precipitate of antimoniate of soda = $NaO + Sb_2O_5 + 7HO$. Consequently it follows that the antimoniate of soda is still less soluble, and I have found that to entirely dissolve one part of this salt, 1200 parts of cold, or 360 parts of boiling water are requisite.

To avoid error in employing the antimoniate of potash as a soda test, sundry precautions are necessary. In the first place, the liquid must contain no other than an alkaline base, as the alkaline earths and most metallic oxides give precipitates with this reagent. Secondly, the liquid must have a neutral reaction or at least possess no perceptible quantity of free potash; carbonate of potash prevents the reaction with soda, partially or entirely, by converting the granular into the gummy antimoniate of potash, which does not precipitate soda salts. The gummy salt on the other hand precipitates the ammonia salts in fine flakes, whilst the granular salt does not affect them. An acid reaction is equally injurious as it precipitates from the solution hydrated antimonic acid or binantimoniate of potash.

As a reagent for soda, the alkaline solution, prepared by boiling the deflagrated mass with 20 parts of water and filtering when quite cold, may be used; but in this case the precaution must be taken that the solution to be tested contains no ammoniacal salts, as the antimonial solution contains both the granular and gummy salt, the latter of which gives a precipitate with ammonia.

KALIUM OXIDATUM SULPHURICUM.

Tartarus Vitriolatus.—Arcanum Duplicatum.—Sal Polychrestus.—Potassæ Sulphas.—Sal Polychrest.—Sulphate of Potash.

FORMULA: $KO + SO_3$.

Preparation.—This salt is seldom prepared directly from its constituents, but is obtained as a residuary product in many preparations; either the neutral salt, as in the purification of potash, or an acid salt, as in making nitric acid from saltpetre. In the first of these cases, only recrystallization is necessary; in the second, it may also be again crystallized (from a solution of bisulphate of potash a neutral salt crystallizes first, *vide* the following article), and then the mother liquor neutralized. It is, however, better to convert the whole of the acid into a neutral salt, by dissolving it in a leaden vessel with six times its weight of water and then gradually adding potashes to the solution until it acquires a feeble alkaline reaction; it is then heated to boiling, and when all the salt which separated during the saturation, has disappeared, filtered, whilst hot, and set in a cool place. After some days the crystals are separated from the mother liquor, the latter evaporated, and this repeated so long as crystals form. The crystals are then dried with a gentle heat. The last portion which crystallizes must be tested to see whether it contains any chloride of potassium, (from the potashes,) this may be partially detected by the form of these crystals, (cubes,) and with certainty on testing the very dilute solution with nitrate of silver; if this causes a white curdy precipitate, chloride of potassium is present, and the portion is set aside from the other.

If neither the common, neutral, nor acid sulphate

of potash is at hand, 1 part of concentrated sulphuric acid is diluted with 9 parts of water in a leaden vessel, and common potashes added, to an alkaline reaction, then heated to boiling, filtered, and evaporated in the preceding manner.—1 Part of concentrated acid requires, according to the purity of the potashes, $1\frac{1}{3}$ to 2 parts; the product will be 2 to $2\frac{1}{3}$ parts.

Recapitulation.—In order to convert the acid sulphate of potash = $(KO + SO_3) + (HO + SO_3)$ into the neutral salt, 1 at. of potashes is necessary; the carbonic acid of the latter is given off with effervescence. As the common potash contains admixtures which also form soluble salts with sulphuric acid, for instance iron, magnesia, &c., the solution must be made slightly alkaline, to precipitate those which may have become dissolved. Leaden vessels are preferable to all others, either for saturating the acid or the acid salt.

Properties.—Neutral sulphate of potash crystallizes in permanent, right rhombic, four or six-sided prisms and pyramids, it is odourless, with a saline slightly bitter and somewhat pungent taste. Cold water dissolves $\frac{1}{10}$, boiling water $\frac{1}{4}$ its weight of the salt; the solution has a neutral reaction. The probable impurities are; *lime* known by the turbidity which oxalate of ammonia causes; *alumina* by the white flocculent precipitate with ammonia, insoluble in excess but soluble in caustic potash; if soluble in caustic ammonia it is *oxide of zinc*, whilst if unaffected by either but dissolved by chloride of ammonium, it is *magnesia*. Should ammonia cause a blue colour in a solution of sulphate of potash, *copper* is present, and the solution after the addition of a few drops of hydrochloric acid, will give a blackish-brown precipitate with sulphuretted hydrogen. If ammonia causes a yellowish or brownish precipitate, it denotes *iron*. *Hydrochloric acid* is detected by nitrate of silver in the diluted solution. It is

possible that the salt may contain *arsenic*, especially if the sulphuric acid was thus contaminated, and the salt had not been re-crystallized. Sulphuretted hydrogen will cause a precipitate of sulphuret of arsenic; if a darker precipitate forms, it must be exhausted with caustic ammonia, and the ammoniacal solution again evaporated; if there now occurs a yellow precipitate which, intimately mixed with neutral oxalate of potash, gives when heated in a narrow test tube a metallic deposit, the presence of arsenic is unquestionable. (*Vide* ACIDUM MURIATICUM, p. 77.)

KALIUM OXIDATUM SULPHURICUM ACIDUM.

Potassæ Bisulphas.—Acid or Bi-Sulphate of Potash.—Sal Enixum.

FORMULA: $(KO + SO_3) + (HO + SO_3)$.

Preparation.—This salt is generally obtained as a secondary product; as, in making nitric acid from saltpetre with 2 at. of sulphuric acid. In order to remove the last traces of nitric acid, the residual saline mass in the retort must be heated to fusion, and retained so, as long as yellow-brownish vapours are given off, and, in order to avoid breaking the retort, is then poured into a well-warmed porcelain dish. On cooling, the salt is powdered and kept in glass bottles.

Failing a nitric acid residue, 10 parts of neutral sulphate of potash are dissolved in a leaden or porcelain vessel with 40 parts of water and 6 parts of concentrated sulphuric acid added to the solution; then evaporated to dryness, during the latter part of the time in a porcelain dish, with constant stirring; a porcelain spatula should be used.

To obtain the salt in crystals, it must not be over-

looked that at first neutral sulphate of potash separates, the bi-salt only forming when the solution contains considerably more than 2 at. of acid. In order to convert the whole into crystals of bi-salt, 2 at. extra of sulphuric acid must previously be added to the solution.

Recapitulation.—The formation of bisulphate of potash by the distillation of nitric acid from saltpetre, has already been explained under the article ACIDUM NITRICUM. If the salt is prepared by direct combination of the neutral sulphate of potash with sulphuric acid, equal atoms of each are required, or to 1090 parts of the former 613 parts of hydrated sulphuric acid, although if commercial acid is employed more will be necessary, it seldom consisting of the simple hydrate. That the first crystals formed consist of the neutral salt, is partly due to its slight solubility, and partly to the slight force with which the second atom of acid is combined with the neutral salt. It is only by a large excess of acid that this is overcome.

Properties.—The bisulphate of potash forms a white crystalline powder, or oblique rhombic tabular crystals, of a very acid taste ; it is odourless, and permanent in the air. Heated it fuses losing at a red heat half its acid, and neutral sulphate of potash remaining. It dissolves in 2 parts of cold and $\frac{1}{3}$ a part of boiling water. Alcohol abstracts the second atom of acid, leaving the neutral salt. Tests for impurities are the same as under the preceding preparation.

KALIUM OXIDATUM SUPERCHLORICUM.

Potassæ Perchloras.—Perchlorate of Potash.

FORMULA : $KO + ClO_7$.

Preparation.—Into a glass flask, capable of holding 30 parts of water, are put 5 parts of chlorate of

potash; the flask is placed with a thin layer of sand in an iron capsule, the latter fitted into a ring furnace and heated. As soon as the salt has liquified, the flask is removed from the capsule, placed in the ring, which must be lower than the surface of the liquid, and exposed to a bright red fire, until the mass which at first boils quietly, begins to thicken and froth up. This occurs according to the strength of the fire, after fusing from half-an-hour to an hour. The flask is then removed from the fire, and when cool, the frothy mass, which will weigh $4\frac{1}{2}$ parts, is boiled with 22 parts of water, and as soon as the whole is dissolved, placed in a cool spot. The salt which separates after 1 or 2 days, is collected in a funnel loosely closed with a glass stopper, washed with a little cold water, again dissolved in 14 parts of boiling water, the solution allowed to remain a few days in the cold, the crystals collected again on a filter and washed with cold water until the liquid which escapes gives no turbidness with nitrate of silver; they are then dried with a gentle heat. The product on the average is half the weight of the chlorate of potash used.

Recapitulation.—When chlorate of potash = $KO + ClO_5$, is heated to fusion, it is decomposed with evolution of oxygen; the quantity of oxygen at first evolved is very trifling, for as it is given off from one portion, it is absorbed by the remainder, which becomes converted into perchlorate of potash. If by the decomposition of a certain portion of the chlorate of potash, all its oxygen entered into combination with the other portion, the product must be more than $\frac{3}{4}$ the weight of chlorate, for

4 at. $KO + ClO_5$, form
3 at. $KO + ClO_7$, and 1 at. KCl.

But, under the most favourable circumstances, only half the chlorate is obtained as superchlorate, the remainder of the oxygen being lost:—

2 at. $KO + ClO_5$, form
1 at. $KO + ClO_7$, 1 at. KCl, and 4 at. O.

3066 Parts of chlorate of potash form on an average 1733 parts of perchlorate of potash, and 400 parts of free oxygen. This loss of oxygen may arise from two causes, either the oxygen is evolved at first more rapidly than the remaining portion can absorb it, or else the perchlorate formed again becomes decomposed into oxygen and chloride of potassium. The latter reason is the more probable, for I have found that the more slowly the heating is continued, (that is the longer time required to reach the thickening point,) the smaller the yield; consequently the fire must be a brisk one. There is but slight reason to fear the breakage of the flask, if it is retained in the iron capsule until the salt is entirely fused, (from the unequal heat at the commencement of the fusion it would often become fractured over a naked fire,) and the ring on which it is placed must be lower than the surface of the fluid, otherwise that part of the glass with which it is in contact, becoming much hotter than the remainder, is cracked as soon as any of the contents is spurted on it. The fusion is continued until all the chlorate of potash is decomposed, which is readily known by quicker boiling, frothing up and thickening of the mass, which suddenly occur. The reason of this thickening is, that chlorate of potash fuses more readily than perchlorate of potash and chloride of potassium, or a mixture of the two. If the heating is continued longer, the perchlorate of potash begins to part with its oxygen, becoming converted into chloride of potassium. By dissolving the mass in water, and allowing it to cool, the chloride of potassium remains in the mother liquor, but to remove it entirely another crystallization and treatment with cold water is necessary. Of course during the purification a small portion of the perchlorate is lost in the mother liquor, and consequently the pro-

duct is seldom more than half the weight of chlorate of potash used.

Properties.—Perchlorate of potash crystallizes in small white glittering grains of a form not exactly determined, is odourless, and possesses a mild scarcely saline taste, becoming sweetish like sugar of milk. At a red heat it fuses, gives off its oxygen, and chloride of potassium remains. It dissolves in 60 parts of water at the ordinary temperature, and in $4\frac{1}{2}$ of boiling water; the solution has a neutral reaction. It is insoluble in alcohol. Adhering *chloride of potassium* is known by the precipitate its solution gives with nitrate of silver. *Chlorate of potash* is detected by supersaturating with dilute nitric acid, when the salt becomes yellow, emitting an odour of chlorine and decolouring litmus paper. The perchlorate of potash is unaffected by dilute nitric acid; whilst the chlorate becomes converted, with evolution of water and chlorine, into chloride of potassium :—

1 at. $KO + ClO_5$ and 6 at. HCl, form
1 at. KCl, 6 at. HO and 6 at. Cl.

KALIUM OXIDATUM TARTARICUM ACIDUM.

Tartarus Depuratus.—Cremor Tartari.—Potassæ Bitartras.—Bitartrate of Potash.—Cream of Tartar.

Formula: $(KO + \dot{T}) + (HO + T)$.

Preparation.—10 Parts of commercially pure tartar are finely powdered, put into a glass flask with 10 parts of pure water, and 1 part of pure hydrochloric acid, spec. grav. 1·130, digested several hours in a sandbath and allowed to cool. After standing 24 hours, the crystalline magma is thrown into a funnel, the bottom of which is loosely closed

with a glass stopper, washed with pure water as long as it passes off acid, or until nitrate of silver solution causes no turbidity, and dried with a gentle heat. The loss will be about $\frac{1}{8}$ the weight of the cream of tartar employed.

Recapitulation.—The cream of tartar of commerce is always contaminated with tartrate of lime, varying from 10 per ct. and upwards; frequently also with copper, which gives it a green tint. The lime comes from the common tartar, the copper from the vessels in which it was purified. Both of these, as well as iron if present, may, without any great loss of material, be separated by means of very dilute hydrochloric acid. To effect this properly, the cream of tartar must be very finely powdered and digested at a gentle heat, with the prescribed quantity of water and hydrochloric acid. The manipulation requires no explanation.

Properties.—Purified cream of tartar forms a snow-white crystalline powder, (the commercial generally occurs in aggregated masses of rhombic prisms,) is odourless and of a feeble acid taste. Its behaviour when heated has already been treated of under the article "KALI. CARBON." 200 Parts of water of the ordinary temperature are required for its solution, whilst only 16 parts of boiling water are necessary; the solution has an acid reaction. Alcohol of 80 per ct. will not dissolve it. Its impurities, as already stated, consist chiefly of tartrate of lime and copper. *Lime* is detected by agitating the cream of tartar with caustic ammonia, filtering, if all does not dissolve, and determining whether oxalate of ammonia causes a white precipitate. By saturating with ammonia the bitartrate of potash is neutralized, and with the tartrate of lime easily and completely dissolved. If the quantity of tartrate of lime is very considerable, a portion of it will remain undissolved; it will, however, in this case contain sufficient to give the reaction with oxalate

of ammonia. If when neutralized with ammonia, hydrosulphuret of ammonia causes a black precipitate, metals are present. The chocolate colour caused by ferrocyanide of potassium in the aqueous solution shows the presence of *copper* (*vide* ACID ACET.); *iron* by the red colour with sulphocyanide of potassium (*vide* BISM. NITR.); or, by the bluish black precipitate caused by tannin in the solution neutralized with ammonia; *sulphuric acid* by the precipitate with nitrate of baryta, insoluble in dilute nitric acid; *hydrochloric acid* by the precipitate with nitrate of silver, also insoluble in dilute nitric acid. In the two latter cases if the reagent causes a precipitate, a mineral acid must be added to try whether it is only a tartrate of silver or baryta, in which case the precipitate will disappear. *Alumina* is also frequently present, and arises from the addition, in process of manufacture from the common tartar, of a little clay, in order to throw down the colouring matter. The alumina cannot be thrown down by ammonia, as its precipitation is prevented by the tartaric acid; but in order to detect it the cream of tartar must be carbonized; boiled with excess of dilute sulphuric acid; filtered, and then supersaturated with ammonia. If alumina be present a white flocculent precipitate of basic sulphate of alumina $= Al_2O_3 + SO_3$ follows, which, washed, dried, and heated with solution of cobalt on charcoal, acquires a blue colour. In many, possibly in all kinds of tartar, a certain portion of tartaric is replaced by *racemic acid*: to determine this, a small portion is neutralized with pure carbonate of potash, taking care not to use an excess, a few ounces of lime water are added, and then a considerable quantity of sal ammoniac; if the precipitate caused by the lime water does not entirely dissolve in the sal ammoniac, *racemic acid* is present. Sal ammoniac dissolves the tartrate but not the racemate of lime. As racemic acid resem-

bles tartaric acid in its chemical constitution and many other respects, is almost always present in it, and removed only with considerable trouble, its presence in cream of tartar, as bi-racemate of potash, can scarcely be looked upon as a falsification.

KALIUM OXIDATUM TARTARICUM NEUTRALE.

Kali Tartaricum.—Tartarus Tartarisatus.—Potassæ Tartras.—Tartrate of Potash.

FORMULA: $KO + \bar{T}$.

Preparation.—40 Parts of water are boiled in a lead or well-tinned copper vessel, 4 parts of carbonate of potash added, and then, constantly stirring, finely-powdered purified cream of tartar, by spoonfuls at a time, as long as it causes an effervescence, and until turmeric paper is no longer changed brown by it. From 11 to 12 parts of cream of tartar will be sufficient. If too much has been added (which is the case if the solution reddens litmus paper), it must be again neutralized by carbonate of potash. The solution exactly neutralized is diluted with 30 parts of water, poured into an earthen dish and allowed to stand at least 3 days in a cool place, then filtered; or (if, as is frequently the case, it filters with difficulty and imperfectly), poured carefully from the sediment, the white of 1 or 2 eggs beaten up added to it, and boiled in a clean iron vessel, either at once to dryness, with constant stirring and great caution towards the end, or else until it acquires a crumbling consistence, when it is spread out on paper, dried with a gentle heat, powdered whilst still warm, and kept in well-closed vessels. The yield is as much or

rather more than the weight of cream of tartar employed.

A portion of the salt thus prepared is dissolved in pure water, and should it yield a very turbid solution, the whole is to be dissolved in twice its weight of water, filtered and evaporated.

Recapitulation.—In order to convert bitartrate of potash (cream of tartar) into the neutral salt, 1 at. of potash must be combined with it; if carbonate of potash is used its acid is given off:—

1 at. $(KO + T) + (HO + \overline{T})$ and 1 at. $KO + CO_2$, form 2 at. $KO + \overline{T}$, 1 at. HO and 1 at. CO_2.

2352 Parts of cream of tartar require 865 parts of carbonate of potash, but as the cream of tartar of commerce always contains some tartrate of lime, the proportion of cream of tartar must either be increased, or the carbonate of potash diminished, in order to obtain a neutral salt. The cream of tartar must be added in small portions on account of the effervescence caused by the evolution of the carbonic acid; at first but little carbonic acid is given off, that liberated from one portion of carbonate combining with another to form bicarbonate, which in its turn becomes decomposed. The tartrate of lime in the cream of tartar partially separates during the saturation, but a considerable portion will be held in solution by the neutral salt, and may be nearly got rid of by diluting considerably with water after the saturation, and exposing the solution for several days to the cold. The lime will in this way be removed sufficiently for medicinal purposes, but not entirely. In order to obtain it chemically pure, the cream of tartar purified by hydrochloric acid must be used. The continued stirring during the neutralization is partly to assist the evolution of the carbonic acid, and also to prevent the lime, when precipitated, from adhering

to the bottom of the pan, and, if the latter be of lead or tin, causing its fusion; if a pure tin pan is employed the slightest relaxation in stirring is dangerous, and if a leaden vessel is not to be had a copper one well tinned is to be preferred. Copper is acted on, as also is iron (as the neutralized solution has no action on iron, a clean iron pan is the most convenient for its evaporation); tin does not hold itself quite indifferent, as after the operation the pan will be found of a gray or black colour where it was in contact with the solution, and suspended in the liquid a fine black powder in which tartaric acid and protoxide of tin may be detected. I have, however, never discovered tin in a state of solution in the liquid, and consequently it cannot be present if neither a tin nor a tinned vessel be employed for its evaporation. A second objection to the employment of tin vessels is their ready fusibility. On a small scale all these objections are obviated by employing a water bath. In making large quantities a clean iron vessel will be found most convenient for evaporating the clear solution, and this may be effected either at once to dryness, or if there be any fear of it charring, only to a stiff pasty consistence, finishing it with a low heat on sieves. The clarification by means of white of egg is due to the property this possesses of coagulating at a certain temperature; on attaining this the whole of the white of egg solidifies, and, enveloping the atoms which cause the turbidity, either precipitates them or forms with them a scum. If the cream of tartar contain copper the iron vessel during the evaporation of the liquid will acquire a coating of this metal, and in this case the pan must be well scoured with sand previous to employing it for a fresh quantity. The salt will then contain iron, but generally the quantity is so trifling as scarcely to affect reagents.

The tartrate of lime may be reserved for the pre-

paration of tartaric acid. If carbonate of potash from potashes is used, it should be tolerably free from sulphates and chlorides, as these salts, owing to the ready solubility of the tartrate of potash, are difficult to separate from it entirely.

Properties.—Neutral tartrate of potash when evaporated to dryness occurs as exceedingly fine crystals, which when rubbed up, form a perfectly white powder; it is odourless and of a slightly bitter saline taste. Exposed to the air it gradually acquires moisture and deliquesces, but the tendency to this is so slight that after keeping it a year in imperfectly closed vessels it has only appeared as a damp powder. Heated, it fuses, becomes black, gives off acid vapours and yields, like cream of tartar, a residue of carbonate of potash and charcoal. Cold water dissolves its weight, boiling water twice its weight of this salt; the solution has a neutral reaction, and yields when slowly evaporated considerable sized rhombic crystals which are anhydrous. In alcohol it is almost entirely insoluble. If it does not give a perfectly clear solution with water, *tartrate of lime* is to be suspected; the filtered liquid which will still retain a portion of the lime, gives in this case a precipitate with oxalate of ammonia; if when filtered from this, a fresh precipitate is caused by phosphate of ammonia, *magnesia* also is present (*vide* AMMON. CHLORAT.). If the residue, after dissolving the salt in water, is not entirely soluble in hydrochloric acid, *silica* is probably present (from the potash). *Iron, copper, alumina, sulphuric and hydrochloric acids* are to be tested for, as under the preceding article. The solution of this, as of most other tartrates, decomposes after some time, forming carbonate of potash and becoming covered with a mouldiness.

KALIUM OXIDATUM TARTARICUM AMMONIATUM.

Potassæ Ammonio-Tartras.—Tartarus Ammoniatus.—Ammoniacal Tartar.—Soluble Tartar.

FORMULA: $(KO + \bar{T}) + (NH_4O + T) + HO$.

Preparation.—4 Parts of finely powdered purified cream of tartar are put into a glass flask with about ten parts of water, to this are added 4 parts of Liquor Ammoniæ, spec. grav. ·960, the flask closed with moist bladder and the contents allowed to digest for several days with frequent agitation. After removing the bladder, the flask is heated, but not to the boiling point, in a sand bath for half-an-hour, the solution filtered, the residue washed with a little hot water, the clear liquor covered with a plate of glass, and set aside in a cool spot to crystallize. After a day or two the crystals which form are separated from the mother liquor, dried on filtering paper without heat, and kept in a closed vessel. To the mother liquor there is added, if necessary, so much finely powdered carbonate of ammonia as shall give it clearly an alkaline reaction, it is then evaporated to half its volume at a temperature lower than that of boiling water, filtered if necessary, the filtrate set in a cool place, and the salt which crystallizes dried between paper; the mother liquor is to be treated in the same way as long as crystals form. The weight of the product will equal that of the cream of tartar employed.

If the salt is not thoroughly soluble in water, it must be treated like neutral tartrate of potash under similar circumstances.

Recapitulation.—Bitartrate of potash when treated with ammonia yields up the half of its acid to the latter, and the two newly-formed salts combined

with 2 at. of water (one of which converts the ammonia into oxide of ammonium) form a very soluble double salt :—

1 at. $(KO + \overline{T}) + (HO + \overline{T})$, 1 at. NH_3, and 1 at. HO, form

1 at. $(KO + \overline{T}) + (NH_4O + \overline{T}) + HO$.

2352 Parts of cream of tartar require 2130 of Liq. Ammoniæ, spec. grav. 0·960 (containing 10 per ct. of pure ammonia); but as a little is given off on warming, a slight excess of the latter is allowed. The neutralization of the cream of tartar takes place without heat, but as there is not enough water to dissolve the newly-formed salt, which partly precipitates, it is warmed. As tartrate of lime is always present a perfectly clear solution cannot be obtained, and hence the necessity for filtering. A small portion of tartrate of lime remains dissolved, but again separates on warming the solution, almost entirely, so that no contamination of tartrate of lime need be feared in the crystals. During the evaporation a small portion of ammonia is evolved, consequently the mother liquor must be neutralized each time, and to avoid diluting it, dry carbonate of ammonia is used. On account of the readiness with which the salt decomposes at a high temperature, the solution must never attain the boiling point, neither, for the same reason must the crystals be dried with heat.

The tartrate of lime, which forms a secondary product, serves for the preparation of tartaric acid.

Properties.—Ammoniacal tartar forms transparent four and six-sided rhombic prisms, smelling faintly of ammonia, and having a cool pungent ammoniacal taste. In the air it decomposes, giving off water and ammonia. Heated, it fuses, giving off ammonia, water, then empyreumatic products, and leaving carbonate of potash and charcoal as a residue. It

dissolves in two parts of cold, and less than its weight of boiling water. The solution has a neutral reaction. The most likely impurities are those enumerated under purified cream of tartar, viz., *Copper*, *Iron*, *Alumina*, *Lime*, *Hydrochloric* and *Sulphuric* acids.

KALIUM OXIDATUM TARTARICUM FERRATUM.

Ferri Potassæ Tartras.—Potassio Tartrate of Iron.

FORMULA OF THAT PREPARED WITH OXIDE OF IRON:

$$4(KO + T) + (FeO + \bar{T}) + 3Fe_2O_3 + \bar{T}.$$

FORMULA OF THAT PREPARED WITH METALLIC IRON:

$$(KO + \bar{T}) + x(FeO + \bar{T}) + x(Fe_2O_3 + \bar{T}).$$

Preparation.—(*a.*) *with Per Oxide of Iron.* 16 Parts of protosulphate of iron are converted, as directed under the article FERRUM OXIDATUM HYDRATICUM (*f.*), into a persalt, and the oxide thrown down with carbonate of potash, the precipitate carefully washed by decantation, the brown magma placed in a porcelain dish with 12 parts of finely powdered cream of tartar, and evaporated, with constant stirring, to the consistence of a soft extract. On cooling, the extract is treated with 36 parts of water and being well stirred, allowed to digest for an hour at the ordinary temperature, then filtered, the residue washed with a little water, and the clear brownish-yellow fluid evaporated to dryness, at a moderate temperature; the resinous mass powdered whilst warm, and kept in well-closed bottles. The yield will about equal in weight the cream of tartar.

(*b*) *With metallic Iron.* — 6 Parts of powdered purified cream of tartar, (or, as ordered in some Pharmacopœias, common tartar), and 1 part of clean iron

filings are placed in a glazed stone or porcelain dish with sufficient water to give the mixture a creamy consistence; a gentle heat is applied if the weather is cold, but not until the end of a week in the summer; the mass is to be frequently stirred, and the water which evaporates replaced as often as the mass becomes stiff. The mixture gradually acquires a darker colour and blackens on the surface; the process is continued so long as gray streaks appear on stirring, and until the mass acquires a uniform black colour; this is generally the case in about 3 or 4 weeks. The mass is then evaporated to dryness at a gentle heat, powdered and kept in well-closed bottles. The yield will be rather less than the cream of tartar and iron employed.

Recapitulation. (*a*)—The formation of the oxide of iron has been already explained under that article. 16 Parts of protosulphate of iron form $4\frac{3}{8}$ parts of anhydrous peroxide of iron, or 2 at. of the first = 3475 parts, correspond to 1 at. of the latter = 1000. Cream of tartar being an acid salt, readily takes up the moist hydrated oxide of iron, forming a brownish-yellow liquid; the iron in this solution is partly reduced to the state of protoxide during the reaction by the cream of tartar. From analysis of the compound it appears that in every 7 at. of peroxide of iron, 1 at. gives off 1 at. or $\frac{1}{3}$ of its oxygen, which causes the formation of 2 at. of protoxide of iron. The liberated oxygen is entirely given off; at least I have been able to discover the separation neither of oxalic, formic, nor carbonic acids, which we should expect to result from the oxidation of tartaric acid. The two atoms of protoxide of iron and the other 6 at. of peroxide unite with 8 at. of bitartrate of potash, to form a double or rather a triple salt consisting of neutral tartrate of potash, neutral prototartrate of iron, and basic pertartrate of iron:—

7 at. Fe_2O_3, form
6 at. Fe_2O_3, 2 at. FeO, and 1 at. O.

then,

8 at. $(KO + \overline{T}) + (HO + \overline{T})$, 6 at. Fe_2O_3, and 2 at. FeO, form
2 at. 4 $(KO + \overline{T}) + (FeO + \overline{T}) + 3(Fe_2O_3 + \overline{T})$, and 8 at. HO.

18820 Parts of cream of tartar, require 7000 parts of peroxide of iron, or 12 parts of the former nearly $4\frac{3}{4}$ of the latter. The evaporation to an extract is to insure the full action of the cream of tartar on the peroxide of iron, and also to cause the separation of any tartrate of lime, on again treating with water; and owing to this tartrate of lime, the product is often less than theory would indicate. By filtration the trifling excess of peroxide of iron is also removed.

(*b*) When cream of tartar, metallic iron, and water come in contact, an action ensues even in the cold; the iron combining with the oxygen of the water forms protoxide, the hydrogen is evolved, and causes the frothing of the mass; the protoxide of iron combines with one atom of the acid from the cream of tartar, to form a white granular precipitate, and the liberated neutral tartrate of potash remains in solution:—

1 at. $(KO + \overline{T}) + (HO + \overline{T})$, and 1 at. Fe, form
1 at. $KO + \overline{T}$, 1 at. $FeO + T$, and 1 at. H.

2352 Parts of bitartrate of potash should require only 350 parts of iron; as, however, this metal always contains carbon and silica, an excess must be taken, but not 1 part of iron to 4 of cream of tartar, as recommended in the Pharmacopœia, for in this case at least one-fourth of the iron remains unacted on. The reaction just described is only the first stage of the process; soon after, that is, as soon as any of the

protoxide of iron has formed and become converted into proto-tartrate of iron, the latter absorbs oxygen from the air, and being partially transformed into persalt combines with a portion of the neutral tartrate of potash; it is from the formation of this persalt that the liquid, at first colourless, acquires its yellow colour, gradually deepening to black. The proto-tartrate of iron becomes more soluble as its oxidation and combination with a part of the neutral tartrate of potash proceeds: this, however, goes on but slowly, so that when all the bitartrate of potash is decomposed a considerable portion remains suspended in the solution. This insoluble portion also contains potash, as a compound consisting of a small portion of tartrate of potash with a large proportion of a tartrate of peroxide and protoxide of iron. Simultaneously with the increased oxidation of the iron, half the tartaric acid separates from the prototartrate :—

2 at. $FeO + \overline{T}$, and 1 at. O, form
1 at. $Fe_2O_3 + \overline{T}$, and 1 at. $\overline{T}$.

This atom of tartaric acid becomes decomposed into volatile products, and by a continued digestion with a gentle heat about $\frac{1}{4}$ the acid in the cream of tartar is thus lost, consequently the yield of well dried salt is generally less than the material used. The magma is now of a black colour, and evaporated to dryness, yields a black mass of a glistening fracture. In this state it will be found that $\frac{2}{3}$ only, or at most $\frac{3}{4}$ of the mass is soluble in water; the solution is black, the residue a lighter or darker greenish-gray. This residue, when $1\frac{1}{2}$ instead of 1 part of iron to 6 parts of cream of tartar has been used, contains a certain portion of iron, but this gradually diminishes as the digestion is continued, not from the formation of more tartrate of iron, but that already present undergoing the same change as it does when exposed to the action of water and air, viz., it becomes grad-

ually changed to insoluble peroxide and protoxide, which remain mixed with the potassio-tartrate of iron, and are the chief cause of the dark colour of the residue. When this salt is treated with water the black colour of the solution is not due, as is generally supposed, to tannin (as tannate of iron), or from other impurities in the tartar, the purified cream of tartar giving the same results as the common, in which by the way I never could discover any tannin; * but the reason of the latter black colour is to be sought for in the proportion in which prototartrate of iron is combined with the pertartrate of iron and tartrate of potash, and the larger proportion of tartrate of potash in the preparation (*a*) causes its much darker colour. The black solution still contains a small portion of the green compound scarcely soluble in water, for on evaporating to dryness this becomes separated and on again treating with water a considerable portion of it remains, and may be filtered off; and it is only after several times evaporating to dryness, redissolving and filtering, that a solution is obtained which, when evaporated to dryness, yields a black glistening mass, entirely soluble in water.

The different residues obtained by treating this preparation with water and evaporating are nearly similar in their constitution, containing potash, tartaric acid, peroxide and protoxide of iron. The black solution is richer in persalt than the residue, but its composition is not constant; for instance, it contains more or less tartrate of potash, combined with the potassio-tartrate of peroxide and protoxide of iron, according to the temperature and length of time employed in its formation; if the digestion has been carried on without any heat, a salt is obtained rich in tartrate of potash, very soluble, and attracting moisture; consequently, in order to obtain a preparation remaining dry in the air, it must

* Tannin can only occur in the preparation if an oaken spatula has been used.

be digested at a gentle heat. An exact formula of the preparation, even disregarding any oxide of iron or metallic iron that may be present, can scarcely be given without entering on a long series of compounds, the composition of which depends on the action of the air, temperature, time employed in washing, &c., and many other accidental circumstances.

The hygroscopic mass prepared by evaporating the solution obtained by digestion without heat, I found of the following composition :—

$$16(KO + \overline{T}),\ 2(FeO + \overline{T}),\ 3(Fe_2O_3 + \overline{T}_2.)$$

That which was permanent in the air, and obtained on dissolving and evaporating several times, gave

$$8(KO + T),\ 1(FeO + \overline{T}),\ 3(Fe_2O_3 + \overline{T}).$$

The residue filtered from the mass when treated with water, gave $2(KO + \overline{T})Fe_2Ox + \overline{T}$; the iron consisting of peroxide and protoxide in undetermined proportions.

Properties.—(*a*) Potassio-tartrate of iron prepared with peroxide is a brownish-yellow, resinous, brittle mass, yielding a greenish-yellow amorphous powder. It is odourless, of a sweetish, mild, ferruginous taste. Exposed to the air for several days the powder attracts moisture, becomes covered with a brownish-yellow varnish-like surface, which however is dry and brittle, and undergoes no further change. Exposed to a strong heat it decomposes without fusing, giving off fumes similar to tartaric acid, and leaving a reddish residue, a mixture of peroxide of iron and carbonate of potash. Water readily dissolves it to a dark, yellowish-brown liquid, having an acid reaction. Alcohol does not dissolve it. Any contamination of *lime* (from impure cream of tartar) is detected by oxalate of ammonia, *copper* by a clean piece of iron.

(*b*) This preparation has a glistening black colour, giving a dark grayish-green powder; its taste and behaviour, when heated, are similar to the pure salt. In the air it attracts moisture, but not sufficiently to become perceptibly damp. Water dissolves only about $\frac{2}{3}$ of it; the insoluble residue is, however, readily taken up by the dilute hydrochloric acid; it is of a variable greenish-brown colour, and, excepting iron (from excess employed) and protoxide of iron, consists of potassio-tartrate of protoxide and peroxide of iron, containing proportionately more protoxide than the compound (*a*); the aqueous solution is black (greenish-black), and contains a salt richer in peroxide (than the residue) and corresponding to the compound (*a*), but containing more tartrate of potash than this does. *Iron* is detected by treating the residue with very dilute hydrochloric acid, when a metallic lustrous residue is left, which, exposed for some time to the air, becomes covered with rust. *Lime* is best detected by heating to redness, when the tartrate is converted into carbonate of lime, then treating the mass with acetic acid, and adding oxalate of ammonia; *copper* by placing a clean piece of iron in the acetic acid solution, or treating the heated mass with ammonia.

KALIUM OXIDATUM TARTARICUM NATRONATUM.

Sodæ Potassio-Tartras.—Potassio-Tartrate of Soda.

FORMULA: $(KO + \bar{T}) + (NaO + \bar{T}) + 8HO$.

Preparation.—3 Parts of crystallized carbonate of soda are dissolved in a lead or well-tinned copper vessel with 20 parts of boiling water, and finely-powdered cream of tartar is added by small portions to the still boiling mixture, which must be

constantly stirred, until the alkaline reaction has nearly disappeared. 4 Parts of cream of tartar are generally sufficient. The liquid is then diluted with 15 parts of water, poured into an earthen vessel, and placed on one side, in the cool, for 3 days, filtered, (if necessary, clarified with white of egg, as directed under the article KALI TART. NEUTR.) and the filtrate evaporated, in a clean iron vessel, until a small portion on removal gives signs of crystallization; it is then poured into glazed stone-ware vessels, and placed in the cool. The crystals after 1 or 2 days are separated from the mother liquor, spread on filtering paper and dried with a very gentle heat; the mother liquor is evaporated as often as crystals form. The last portions are generally yellow coloured, and require a second crystallization; if this is only a small portion it is better to keep it for a fresh quantity of the preparation. As an average, about $4\frac{1}{2}$ parts of the potassio-tartrate will be yielded.

Recapitulation.—This is merely a repetition of that under KALI TART. NEUTR.; the soda neutralizes the second atom of acid in the cream of tartar, and the carbonic acid is given off. The tartrate of soda thus formed gives, with the tartrate of potash which remains, and a portion of water, a very soluble crystallizable double salt:—

1 at. $(KO + \overline{T}) + (HO + \overline{T})$, and 1 at. $NaO + CO_2 + 10HO$, form

1 at. $(KO + \overline{T}) + (NaO + \overline{T}) + 8HO$, 1 at. CO_2, and 3 at. HO.

2352 Parts of cream of tartar require 1790 parts of crystallized soda for their saturation; these relative weights vary according to the state of purity of the salt (tartrate of lime being frequently found in the cream of tartar, and sulphate of soda in the carbonate of soda). By crystallization the foreign

salts are removed the sulphate of soda remaining in the mother liquor, whilst such portions of tartrate of lime as were not precipitated during the neutralization will separate on evaporating the mother liquors. For the remainder I must refer to the article KALI. OXID. TART. NEUTRALE.

If the cream of tartar contain much racemic acid a considerable loss of crystallized potassio-tartrate of soda will result, and the mixture contain a large quantity of syrupy mother liquor; for the racemic acid forms with difficulty a double salt of potash and soda.

Properties.—Potassio-tartrate of soda forms transparent, right, rhombic, 6 and 12 sided prisms, often of considerable size. It is odourless, of a mild, saline, cooling taste. It is unalterable in the air at the ordinary temperature; in the summer it sometimes gives the very slightest indication of efflorescence; at a moderate temperature it fuses in its water of crystallization, again becoming solid; if the heat is increased it again fuses, but the tartrate of potash now decomposes, and leaves a mixture of carbonate of potash, carbonate of soda, and charcoal. 1 Part of the salt dissolves in $2\frac{1}{2}$ parts of cold water, whilst it requires scarcely its weight of boiling; the solution has a neutral reaction. Alcohol takes up only traces of it. Its most probable impurities are *iron*, *copper*, *alumina*, *lime*, *magnesia*, *sulphuric* and *hydrochloric acids*, the tests for which are given under KALI. OXID. TART. ACID. An adulteration with *alum* is detected by its sweetish astringent taste and acid reaction, whilst *borax* gives an alkaline taste and reaction. Alum and borax when heated both liquify in their water of crystallization, then froth up to a spongy mass, which fuses together, at a high temperature, without blackening.

KALIUM OXIDATUM TARTARICUM STIBIATUM.

Antimonii et Potassæ Tartras.—Potassio-Tartrate of Antimony.—Tartar Emetic.

FORMULA: $(KO + \overline{T}) + (Sb_2O_3 + \overline{T}) + 2HO$.

Preparation.—5 Parts of finely-powdered cream of tartar and 4 parts of pure oxide of antimony (*vide* STIBIUM OXIDATUM) are placed with six parts of pure water in a flask capable of containing 50 parts water, or in an equally capacious porcelain dish (with large quantities a leaden vessel may be used); the whole digested at a temperature of from 140°—180° Fah., and constantly shaken, or stirred with a porcelain rod (the water which evaporates to be, if necessary, replaced) for from 1 to 3 hours; 30 parts of water are then added, the mixture boiled for ½ an hour, and filtered whilst hot into a glass or porcelain vessel. The crystals, which separate after several days, are freed from the mother liquor, which is evaporated to half its bulk, filtered, and allowed to crystallize; this is repeated so long as crystals form. When the mother liquor yields no more crystals, and acquires a strong acid reaction, it is diluted with water, saturated by digestion with a fresh quantity of oxide of antimony, filtered and again evaporated to crystallization. The crystals are collected, spread out on paper to dry in the air, finely powdered and digested for 1 day, frequently agitating, with fifteen times its volume of water in a flask: the solution is then filtered, evaporated to crystallization, and the purified dried salt kept in well-closed bottles. It should weigh from 6 to 7 parts.

The "Vitrum antimonii," which is sometimes ordered, gives but an indifferent preparation, and should not be employed. Neither can I give any

preference to the method of heating sulphuret of antimony, nitre, and sulphuric acid together, exhausting the mass with water and treating the residue with cream of tartar.

Recapitulation.—In a similar manner to soda and ammonia, the oxide of antimony saturates the second atom of acid of the cream of tartar, forming a double salt of neutral tartrate of potash and basic tartrate of antimony, which in a crystallized state contains 2 at. of water:—

1 at. $(KO + \overline{T}) + (HO + \overline{T})$ and 1 at. $Sb_2O_3 + HO$, form

1 at. $(KO + \overline{T}) + (Sb_2O_3 + \overline{T}) + 2HO$.

2352 Parts of cream of tartar require 2024 parts of hydrated oxide of antimony. The digestion must first be made in a creamy state, in order that the particles may be in close contact, and only boiled with a large quantity of water when the double salt is formed, in order to dissolve the latter; the filtration must take place whilst hot, as a large quantity of salt separates on cooling. An entire solution of the creamy mass is seldom effected; the residue is either tartrate of lime (from impure cream of tartar) or excess of oxide of antimony, as the exact quantity of this required can never be calculated owing to the different degrees of purity of the cream of tartar. The last portions of tartar emetic formed are yellowish, owing to a trace of iron. After obtaining two or three crops of crystals a syrupy mother liquor generally remains, which has a very acid reaction and yields no more crystals. This arises from the formation of a double salt of neutral tartrate of potash and neutral tartrate of antimony $= (KO + \overline{T}) + (Sb_2O_3 + 3\overline{T})$, and is due to an excess of cream of tartar; it necessitates at the same time the separation of free neutral tartrate of potash:—

3 at. $(KO + \bar{T} + HO + \bar{T})$ and 1 at. Sb_2O_3, form
1 at. $(KO + \bar{T}) + (Sb_2O_3 + 3\bar{T})$, 2 at. $KO + \bar{T}$ and 3 at. HO.

To use up this mother liquor, it is diluted with water and boiled with a fresh quantity of oxide of antimony, which converts the neutral into the basic tartrate of antimony, and this, with the neutral tartrate of potash present, forms tartar emetic :—

1 at. $(KO + \bar{T}) + (Sb_2O_3 + 3\bar{T})$, 2 at. $KO + \bar{T}$, and 2 at. Sb_2O_3, form
3 at. $(KO + \bar{T}) + (Sb_2O_3 + \bar{T})$.

The mother liquor might at once be saturated with carbonate of potash, but this would cause a great loss of tartrate of potash ; for,

1 at. $(KO + \bar{T}) + (Sb_2O_3 + 3\bar{T})$, 2 at. $KO + \bar{T}$, and 2 at. $KO + CO_2$, form
1 at. $(KO + \bar{T}) + (Sb_2O_3 + \bar{T})$, 4 at. $KO + \bar{T}$, and 2 at. CO_2.

The second crystallization of the salt is to separate the last traces of tartrate of lime, and also any traces of copper or iron. To avoid this second crystallization, the cream of tartar before using must be purified with hydrochloric acid.

Properties. Cream of tartar crystallizes in transparent right rhombic (not tesseral) octohedra, which are odourless, of a feebly sweetish taste, becoming afterwards nauseously metallic. In the air the crystals, from loss of water, become opaque and very brittle. Heated in a test tube the crystals decrepitate, and, without entirely fusing, give off their water with a continuous crackling ; almost at the same time the salt acquires colour, decomposes with the evolution of empyreumatic matter, and becomes black ; the carbonaceous mass is a mixture of carbonate of potash, reduced anti-

mony, and carbon; heated in the air the carbon glows, the antimony fuses to globules, at the same time becomes partially oxidized and gives off white fumes of oxide of antimony. Tartar emetic dissolves in 14 parts of cold and 2 of boiling water; the solution has an acid reaction. Alcohol does not dissolve it. Its aqueous solution must not be rendered turbid by oxalate of ammonia, ferrocyanide of potassium, chloride of barium, or nitrate of silver. If oxalate of ammonia causes a precipitate *lime* is present; a brown precipitate with ferrocyanide of potassium indicates *copper*, a blue one *iron;* the presence of copper is rendered certain if, on treating the cream of tartar with liquor ammonia, a permanent blue solution is formed, that of iron when sulphocyanide of potassium causes a red colour, (*vide* BISM. NITR.). Chloride of barium indicates *sulphuric acid*, and nitrate of silver *hydrochloric acid* when they cause precipitates. The presence of *arsenic* is not to be feared even if the antimony contained it, as it will all remain in the mother liquor. To test the tartar emetic for arsenic, the following method is the best:—About half an ounce of it is finely powdered, dried with a gentle heat, mixed with its weight of nitre, and the mixture thrown by degrees into a red-hot crucible. In a quarter of an hour the crucible is withdrawn from the fire, allowed to cool, its contents exhausted by boiling with water, the turbid liquor supersaturated with pure dilute sulphuric acid, and the whole evaporated nearly to dryness; the mass is then softened with water, filtered, and a few bubbles of sulphuretted hydrogen passed through it, sufficient to allow of its being detected, after agitation, by the smell, or paper saturated with solution of acetate of lead. The yellowish-red precipitate caused by sulphuretted hydrogen is separated by filtering, the clear liquor heated until every trace of sulphuretted hydrogen is removed, allowed to cool, and a solution

of sulphurous acid added by drops until the odour of it is perceptible even on shaking for some minutes; again heated to remove the excess, and sulphuretted hydrogen passed through the cooled solution. After this is saturated and allowed to stand in a moderately cool place for one day, the precipitate which forms is collected on a filter (if there be none the tartar emetic is free from arsenic), washed well, and dissolved in liquor ammonia by pouring this over the filter as it lies in the funnel; the ammoniacal fluid is collected in a watch glass and evaporated to dryness. The yellow residue is intimately mixed with 6 times its weight of well-dried neutral oxalate of potash, the mixture poured into a narrow test tube, and heated over a spirit lamp. It gradually becomes gray, fuses, and evolves a vapour which partly covers the upper portion of the tube, as a gray ring of a metallic lustre, and is partly evolved, giving off a smell resembling garlic.

This is certainly rather circumstantial, but to detect arsenic with any degree of accuracy, in tartar emetic, the removal of the antimony must be carefully effected, as small quantities of arsenic with an excess of antimony cannot be discovered with certainty. By deflagrating with nitre the oxide of antimony is converted at the cost of the oxygen of the nitric acid, into antimonic acid, and any arsenious acid that may be present into arsenic acid, both of which acids remain combined with potash; the elements of the tartaric acid form carbonic acid and water. A portion of this carbonic acid unites with that portion of the potash which has entirely lost its nitric acid:—

1 at. $(KO + C_4H_2O_5) + (Sb_2O_3 + C_4H_2O_5)$ and 3 at. $KO + NO_5$, form
1 at. $KO + Sb_2O_5$, 6 at. CO_2, 4 at. HO, 2 at. $KO + CO_2$, 1 at. $KO + NO_3$, and 2 at. N.

Thus carbonic acid, water, and nitrogen are

evolved; whilst antimoniate of potash, carbonate of potash, and nitrite of potash form the residue. 4152 Parts of anhydrous tartar emetic require 3795 parts of saltpetre. The slight excess of nitre by using equal proportions of the two salts is of no ill consequence, but rather insures entire oxidation, and becomes converted at a red heat into nitrite of potash with evolution of oxygen. The explanation remains the same if, in the preceding formula, we consider the oxide of antimony partly replaced by arsenious acid and the antimonic by arsenic acid. On treating the heated mass with excess of sulphuric acid, this absorbs all the potash, precipitating the antimonic acid almost completely, whilst all the arsenic acid remains in solution with the sulphate of potash, carbonic and nitrous acids being evolved; the evaporation to dryness which follows, insures the entire evolution of the nitrous acid. If now, on diluting the mass with water and filtering, sulphuretted hydrogen is passed through the solution, (acid from the excess of sulphuric acid,) the small excess of antimonic acid present is precipitated as the highest sulphuret of antimony, and the arsenic acid only when it is reduced to arsenious acid. This reduction is caused by the sulphurous acid whilst being converted into sulphuric acid:—

1 at. As_2O_5 and 2 at. SO_2, form
1 at. As_2O_3 and 2 at. SO_3.

Previous to the addition of the sulphurous acid, and after removing the sulphuret of antimony, the sulphuretted hydrogen still in the solution must be driven off, otherwise the action of the former (sulphurous acid is exerted on the sulphuretted hydrogen, converting it into sulphur and water:—

1 at. SO_2 and 2 at. HS, form
3 at. S and 2 at. HO.

On the other hand it is quite evident that all traces

of the sulphurous acid must be removed by heating previous to treating it a second time with sulphuretted hydrogen. The precipitate now caused by sulphuretted hydrogen is a pure yellow, and has the composition of orpiment = As_2S_3 :—

1 at. As_2O_3 and 3 at. HS, form
1 at. As_2S_3 and 3 at. HO.

To remove it from the filter without loss, it is dissolved in liquor ammonia, and this driven off by evaporation. On heating with dry neutral oxalate of potash, ($KO + C_2O_3$), the sulphuret of arsenic is reduced; the arsenic is evolved and known by the characteristics previously given, the sulphur combines with the potassium and the oxygen of the potash with the oxalic acid, which is converted into gaseous carbonic acid, and evolved with the arsenic :—

3 at. $KO + C_2O_3$ and 1 at. As_2S_3, form
3 at. KS, 6 at. CO_2, and 2 at. As.

The grayish-black colour which the mixture acquires after heating to redness arises from the decomposition of the excess of oxalate of potash present; this acording to theory should separate into carbonate of potash and carbonic oxide, and consequently form a white residue :—

1 at. $KO + C_2O_3 = 1$ at. $KO + CO_2$,
and 1 at. CO;

but a portion of the carbonic oxide decomposes into carbonic acid and carbon, the latter of which remains mixed with the carbonate of potash, so long as oxygen is wanting for its combustion.

Lastly, not to leave the faulty part of the previous method unnoticed, I must remark that when tartar emetic contains arsenic, a garlic odour is generally evolved during the deflagration, this, although due to a loss of arsenic, leaves the presence of this metal

without doubt. The greater part of the arsenic escapes this momentary reduction and volatilization, and will with certainty be found in the latter part of the process. By the first treatment with sulphuretted hydrogen, for the purpose of removing the last traces of antimony, a small portion of the arsenic also is thrown down; the second action of the sulphuretted hydrogen is not on this account to be omitted, as the solution still contains the larger portion of the arsenic. I should, however, recommend that the first precipitate be tested by reduction with oxalate of potash, and if arsenic is discovered in it, the second precipitation with sulphuretted hydrogen is unnecessary. The antimony as well as the arsenic is separated from its sulphurets in the metallic taste, but the former is not volatilized by the heat to which the test portion is subjected, and therefore it yields no metallic sublimate; but even if this should happen, there will be no garlic odour of arsenic. The sulphuret of antimony is in the highest state of sulphuration = Sb_2S_5, and as this, gives off 2 at. of sulphur below the temperature at which the oxalate of potash can exert any action, a sublimate of sulphur is always formed under the circumstances. The separation of any arsenic present will not be in the least affected, for all the sulphur will be given off before any of the metal is evolved.

KALIUM SULPHURATUM.

Potassii Sulphidum.—Hepar Sulphuris Kalinum.—Potassium Sulphuretum.—Sulphuret of Potassum.—Liver of Sulphur.

FORMULA: $2KS_3 + (KO + 2SO)$.

Preparation.—(a.) The pure compound. According to the directions in most Pharmacopœias, the liver of sulphur is really a tersulphuret of potassium =

KS_3; and the relative proportions here given are the same. A narrow-necked glass flask is only $\frac{1}{3}$ filled with an intimate mixture of 5 parts of pure carbonate of potash and 3 parts of washed sulphur; the flask is placed on a thin layer of sand with which it is surrounded to about half its depth, then heated, at first gently, but when the mixture begins to fuse, more strongly, until the whole forms a liver-coloured, thickish but entirely fluid mass, which no longer puffs up. To determine with greater certainty whether the reaction is finished, a portion is withdrawn on a glass rod and treated with water; if it entirely dissolves without the precipitation of any yellow powder, all the carbonate of potash is decomposed, otherwise the fusion must be continued. The flask is now removed from the fire, closed with a cork, or with bladder, when cold broken, the contents coarsely powdered and kept in a well-closed bottle. The yield is somewhat over 6 parts.

b. The common preparation. 2 Parts of carbonate of potash from potashes, or if the Pharmacopœia permits it common potashes, are mixed with 1 part of pounded sulphur in a strong cast iron pot, which should not be more than $\frac{1}{3}$ full; the pot is then placed on a bright fire, and when the mixture begins to fuse, closed with a cover, well stirred from time to time with an iron spatula, heated until it is entirely liquid, and no longer puffs up; a portion is then tested as in the preceding, by shaking with water; if no yellow powder separates, the fused mass is quickly poured into a cold iron vessel which has been previously oiled, and the latter well covered. As soon as the mass has sufficiently cooled to become brittle, it is coarsely powdered and kept in a well-closed bottle. If the potash or carbonate of potash was not moist, $2\frac{1}{3}$ parts of liver of sulphur will be produced.

The preparation of liver of sulphur in quantity, which necessitates the employment of open vessels,

requires some precaution, as the mass so soon as it liquifies readily ignites at the sides, and the sulphurous acid thus evolved renders it very dangerous to the workmen; if iron vessels are employed they are, unless very thick, soon eaten through, whilst the liability to breakage prevents the use of earthen vessels. I find these evils may be altogether avoided if the so-called wet method is followed. For this process 2 parts of carbonate of potash, 1 part of sulphur, and 2 parts of water are heated to boiling, which is continued so long as the mixture puffs up. When on withdrawing a portion and mixing with water, it ceases to give a precipitate of sulphur, the heat is raised until the mass is not only brittle on cooling, but forms a limpid fluid in the pot, which is then withdrawn from the fire and the contents poured into another vessel, the surface of which has been rubbed with oil; when cold the mass is broken up, &c., &c. If the mass when treated with water still gives off sulphur, ½ a part of water must be added, and again boiled. The objection to this process is the greater time required.

If, instead of tersulphuret, the highest or pentasulphuret = KS_5 is required, the proportions are 5 parts of pure carbonate of potash, to 4½ parts of sulphur; or, 2 parts of caustic potash and 1½ parts of sulphur.

Recapitulation.—If carbonate of potash and sulphur are heated in the proportion to form the tersulphuret, 2 at. of potash give their oxygen to 2 at. of sulphur; the hyposulphurous acid thus formed combines with 1 at. potash to hyposulphite of potash, the 2 at. of potassium with 6 at. of sulphur form tersulphuret of potassium and the carbonic acid is evolved, causing the puffing up:—

3 at. $KO + CO_2$ and 8 at. S, form
2 at. KS_3, 1 at. $KO + S_2O_2$, and 3 at. CO_2.

2595 Parts of pure carbonate of potash require

1600 parts of sulphur; if potashes are employed the sulphur must be diminished by $\frac{1}{5}$ on account of the impurities they contain.

If the mixture is such as to produce the highest sulphuret, 10 at. of sulphur combine with the 2 at. of potassium:—

3 at. $KO + CO_2$ and 12 at. S, form
2 at. KS_5, 1 at. $KO + S_2O_2$, and 3 at. CO_2,

Or, 2595 parts of pure carbonate of potash require 2400 parts of sulphur. On account of the puffing up that the evolution of carbonic acid causes, capacious vessels must be used; for small quantities glass flasks are most convenient, and on the large scale cast-iron vessels. As soon as the mass becomes quietly fluid, it is well, previous to removing from the fire, to try if it is perfectly soluble, free from uncombined sulphur.

If the precaution is taken that it does not ignite (*i.e.* a flask is used), little or no sulphuric acid will be formed; if, however, wide open vessels are employed, this can scarcely be prevented, and the hyposulphite of potash by absorbing oxygen, becomes partially or entirely converted into sulphate of potash and the excess of sulphur is evolved as sulphurous acid:—

1 at. $KO + S_2O_2$ and 3 at. O, form
1 at. $KO + SO_3$ and 1 at. SO_2.

It is also possible that sulphite of potash may be formed, and according to the length of time it burns, a variable quantity of hyposulphite, sulphite and sulphate of potash will be formed in the preparation. Sulphuret of potassium, through combustion, undergoes the same change into sulphite and sulphate of potash as the hyposulphite of potash does. Consequently liver of sulphur, although made with pure materials, should when containing much sulphate be rejected as faulty; this is, however, seldom done,

as in employing open vessels the contamination can scarcely be avoided. In the common sulphuret of potassium (as used for baths) an additional quantity of sulphate occurs from that contained in the pot-ashes employed.

The formation of sulphate of potash is least when the wet method is employed. On the small scale it is least advantageous, as the short time required for the water to evaporate renders it necessary to dilute it two or three times. On the large scale, however, the proportionably longer time required to evaporate the equal weight of water from the carbonate of potash, will generally be sufficient to dissolve the sulphur. A portion which on testing is found to be perfectly combined, gives, when evaporated until it becomes brittle on cooling, a liver containing $\frac{1}{7}$ its weight of water; to remove this water the mass must be heated until it loses its stiff consistence, that is, until it commences really to fuse.

Properties.—Liver of sulphur is a hard brittle mass, of a yellow colour with a tinge of green; when quite dry it is nearly odourless, of a bitter strongly alkaline and hepatic taste. In the air it attracts moisture and deliquesces, but becomes in this way decomposed, evolving sulphuretted hydrogen whilst sulphur separates; for this reason all liver of sulphur when in contact with the air gives off the odour of rotten eggs. The sulphuretted hydrogen is formed by the decomposition of the water, with the hydrogen of which a portion of the sulphur combines, whilst the greater part separates as such, or in combination with a trace of sulphuretted hydrogen, like milk of sulphur, and consequently is of a yellowish-white instead of a yellow colour. At the same time the potassium becomes oxidized from the oxygen of the water, and the potash thus formed unites with the carbonic acid of the atmosphere:—

1 at. KS_3, 1 at. HO, and 1 at. CO_2, form
1 at. $KO + CO_2$, 1 at. HS, and 2 at. S.

At the same time the free oxygen of the atmosphere, acting on another portion of the sulphuret of potassium, causes the formation of hyposulphite of potash, and the separation of free sulphur; (this is yellow and crystalline):—

1 at. KS_3, and 3 at. O, form
1 at. $KO + S_2O_2$, and 1 at. S.

The sulphuret of potassium when entirely deliquesced and no longer smelling of sulphuretted hydrogen, consists of carbonate and hyposulphite of potash, and uncombined sulphur. The proportions of hyposulphite and carbonate of potash formed by the contact of the air, are however inconstant; the richer the preparation in sulphur the less carbonate is formed, and *vice versâ;* for instance with the tersulphuret = KS_3 almost all is changed to carbonate, whilst in pentasulphuret = KS_5 on the other hand, the greater portion is converted into hyposulphite; the sulphuretted hydrogen evolved in the first instance during the decomposition must be far more than in the second. This explains why liver of sulphur kept in badly closed bottles or vessels frequently opened gradually acquires a white surface (of precipitated sulphur). When heated, the preparation acquires a liver-brown colour (hence its name) and melts; at a higher temperature the sulphur volatilizes, and, if the air has access becomes converted into sulphurous acid, which finally remains (or partially remains) in the mass as sulphate of potash. Liver of sulphur is dissolved by water with the greatest facility, but requires a larger quantity for its solution when it contains much sulphate of potash; a white deposit unaltered by a large quantity of water denotes the presence of *silica* or *alumina* (from the potash) a black or gray one is probably *iron* (sulphuret of iron), a yellow one *free sulphur*. Alcohol of 80 per ct. dissolves the sulphuret of potassium from the liver of sulphur, leaving the hyposulphite, sulphite, and

sulphate of potash undissolved; all the *chloride of potassium*, (or at least most of it,) the *carbonate of potash*, and other impurities will be found in the residue. The aqueous and alcoholic solutions have a strongly alkaline reaction. *Carbonate* of *potash*, which sometimes comes from using an excess of potash, and sometimes from the age and frequent exposure of the preparation to the air, is detected by the addition of lime water, which it renders turbid. If the liver of sulphur when treated with dilute sulphuric acid effervesces without evolving any sulphuretted hydrogen, it must be thrown away as useless.

LITHIUM CHLORATUM.

Lithii Chloridum.—Lithium Muriaticum.—Chloride of Lithium.

FORMULA: LiCl.

Preparation. (*a*)—*From Triphylin.* 6 Parts of hydrochloric acid spec. grav. 1·130, and 1 part of nitric acid spec. grav. 1·2 are placed in a flask capable of containing 20 parts of water, and with constant agitation 3 parts of finely powdered triphylin are added; the mixture is digested in a sand bath until the liquid, at first brown, is converted into a clear yellow, and the whole poured into a capacious earthen dish, diluted with from 8 to 12 times its weight of water, and precipitated with excess of liq. ammonia. From 8 to 9 parts will be sufficient if its spec. grav. is 0·960. After standing for some days the voluminous precipitate is collected on a filter, and when drained as much as it will must be pressed, returned to the dish, again treated with water, and the process repeated once or twice, or until the wash water no longer has a saline taste. The liquids

are filtered and evaporated to dryness in a porcelain dish. The dry salt is put into a retort, having a short neck, the latter placed on a thin layer of sand in an iron pot and surrounded with sand to the depth of the salt; a receiver is attached without any luting, and a moderately strong heat applied from 1 to 4 hours, according to the quantity of the salt. On cooling the retort is broken, the sublimate (sal ammoniac) removed from the upper part, and the residual saline mass dissolved in pure water; the solution is rendered alkaline with caustic ammonia, treated with oxalate of ammonia as long as it causes a precipitate, allowed to deposit, filtered, evaporated to dryness in a porcelain dish, and heated in a platinum crucible to drive off all the ammoniacal salts. The heated mass is again dissolved in pure water, filtered, the filtrate evaporated to dryness and the salt, still warm, placed in a well-closed bottle. The product from 56 parts of triphyllin will be 10 or 12 parts.

(*b.*) *From Sulphate of Lithion.* 8 Parts of crystallized sulphate of lithion are dissolved in 80 parts of distilled water, and 15 parts of chloride of barium also in 80 parts of water; the greater part of the first solution is mixed with the latter, and the remainder added gradually in very small portions so long as it causes a precipitate. Care must be taken that neither the chloride of barium nor sulphate of lithion remains in excess. When the precipitate has subsided it is filtered, washed with distilled water, the filtrate evaporated to dryness and kept in well-closed bottles. About 5 parts will be thus produced.

Recapitulation.—(*a*) The Triphyllin is a basic terphosphate of protoxide of iron (peroxide ?), protoxide of manganese and lithium, which, according to the analysis of Fuchs, consists in 100 parts of 41·47 phosphoric acid, 48·57 protoxide of iron, 4·70 protoxide of manganese, 3·40 lithium, 0·53 silica, and 0·68 water. Excepting the silica, it is entirely

soluble in hydrochloric acid, but the nitric acid is added to convert the iron into per-oxide, or rather per-oxide and per-chloride, because only the per-phosphate of iron is entirely precipitated by ammonia. That chlorine, nitric oxide and water are formed on mixing hydrochloric and nitric acids, has been explained already several times. The above mixture, 6 parts of hydrochloric acid and 1 part nitric acid, contains a considerable excess of the former. When finely-powdered mineral is added to this mixture, it dissolves first of all in the hydrochloric acid; it must not be added in large portions, or from absorbing the acid slowly hard lumps will be formed, which adhere to the bottom of the glass, and render it liable to fracture, and they are afterwards dissolved only with difficulty. By continued digestion the brownish colour of the fluid changes (with the evolution of brown vapours of hyponitric acid) into yellow, from a portion of the chlorine, which is liberated by the nitric acid, decomposing some of the water, the oxygen of which converts the protoxide into peroxide of iron, and the hydrogen again combines with the chlorine to hydrochloric acid. The peroxide of iron having a greater capacity for combination than the protoxide, is capable of taking down both the phosphoric acid combined with the lithion as well as its own, and chloride of lithium is thereby formed. As the iron remains combined with the phosphoric acid its increased oxidation may be explained, by saying that the nitric acid merely imparts to the protoxide a portion of its oxygen, or, that the free chlorine abstracts iron from the protoxide, forming perchloride, the remainder becomes peroxide, whilst the chloride of iron changing constituents with the phosphate of lithion, chloride of lithium and perphosphate of iron are the results:—

1 at. $3\,LiO + P_2O_5$, and 1 at. Fe_2Cl_3, form
3 at. LiCl and 1 at. $Fe_2O_3 + P_2O_5$.

The solution, when all the iron is converted into oxide, contains chloride of lithium, perphosphate of iron, and proto-phosphate of manganese. The two latter salts, together with any alumina, are entirely thrown down by ammonia, their solvent (hydrochloric acid) being withdrawn, and sal ammoniac formed. The brown precipitate, which at the same time contains that portion of the mineral undissolved by the hydrochloric acid (silica), separates with difficulty, and must, therefore, be filtered and pressed; in order to obtain as much as possible of the salt it is again treated with water. As a portion of the precipitate becomes forced through the pores of the strainer, the liquid requires filtering previous to evaporation. To prevent the loss of the sal ammoniac, which is present in considerable quantity, a retort is employed in driving it off. The residual mass which still contains traces of chlorides of ammonium and calcium (the latter from carbonate of lime generally present in the mineral), is treated with ammonia to effect its entire neutralization and the precipitation of any traces of perphosphate of iron; with oxalate of ammonia to remove the lime; then evaporated to dryness and heated to free it from any adhering ammoniacal salts.

(*b*) Sulphate of lithion and chloride of barium are entirely decomposed in their aqueous solutions into sulphate of baryta and chloride of lithium :—

1 at. $LiO + SO_3 + HO$, and 1 at. $BaCl + 2HO$, form 1 at. LiCl 1 at. $BaO + SO_3$, and 3 at. HO.

For 795 parts of crystallized sulphate of lithion 1524 parts of crystallized chloride of barium are requisite.

Properties.—Chloride of lithium thus prepared is a white, odourless, crystalline powder, of a pungent saline taste resembling common salt; in the air it attracts water with the greatest avidity and delequesces; heated to redness it fuses without change.

Water and alcohol readily dissolve it, the solutions have a neutral reaction, the latter one burns with a carmine red flame. If its aqueous solution is rendered turbid by oxalate of ammonia, *lime* is present, and a precipitate afterwards caused in the filtered solution by phosphate of ammonia denotes *magnesia*. If a solution of sulphate of magnesia causes a precipitate in the liquid to which ammonia has been added, it contains *phosphoric acid*. The precipitate in either of the two last-mentioned cases is phosphate of ammonia and magnesia (*vide* AMMON. CHLORATUM). Ammonia precipitates any *iron* that may be present as brown flakes; if these contain perphosphate of iron they have a more transparent appearance than the pure oxide; on treating with hydrosulphate of ammonia they instantly assume the black colour characteristic of iron. On agitating the precipitate caused by solution of caustic potash, filtering, and adding solution of sal ammoniac, a precipitate or turbidness is due to *alumina* (*vide* CALC. CHLOR.). *Sulphuric acid* is detected by chloride of barium. If it is not entirely soluble in absolute alcohol, *chloride of sodium* is probably present; to determine this, exhaust the insoluble portion with absolute alcohol, dry and heat it on a platinum wire before the blowpipe; if soda be present the flame will be an intense yellow colour. If the residue agitated with water gives, on the addition of tartaric acid, a crystalline precipitate, *potash* is present. If it has any *chloride of ammonium* adhering to it the addition of caustic potash will cause the odour of ammonia to be evolved.

MAGNESIUM OXIDATUM PURUM.

Magnesia Usta.—Oxide of Magnesium.—Calcined Magnesia.

FORMULA: MgO.

Preparation.—A convenient quantity of commercial carbonate of magnesia in small lumps (not finely powdered) is placed in an earthen crucible which may be nearly filled, and the latter, covered, is placed in a good wind furnace. So soon as the crucible is red hot, its contents are from time to time carefully stirred with a clean iron spatula, and when the interior portion has also acquired this temperature, a small quantity is withdrawn, and, when cool, shaken with sulphuric or hydrochloric acid. If this causes an evolution of gas, the heat must be continued until a small portion dropped into a glass of dilute acid quietly sinks to the bottom, and after a few minutes dissolves without the slightest evolution of gas. The contents of the crucible are now emptied on a clean iron or copper plate, and before they are quite cool placed in a well-stoppered bottle; the crucible in the mean time is filled with a fresh portion and the heating proceeded with. 9 Parts of carbonate of magnesia yield about 4 parts of calcined.

Recapitulation.—The commercial carbonate of magnesia is a basic salt, consisting of 4 at. magnesia, 3 at. carbonic acid, and 4 at. water, which may be considered a combination of 3 at. neutral hydrated carbonate of magnesia and 1 at. hydrate of magnesia. When heated to redness, the carbonic acid and water are given off, and the pure magnesia remains:—

1 at. 3 ($MgO + CO_2 + HO$) + ($MgO + HO$), give 4 at. MgO, 3 at. CO_2, and 4 at. HO.

2307 Parts of carbonate of magnesia yield 1032 parts of calcined. The water and carbonic acid are given off most readily when the preparation is in moderate-sized lumps. In testing for carbonic acid the dilute acid must not be added until the magnesia is nearly cool, otherwise a hissing is caused which may readily be mistaken for an effervescence. The magnesia should also be added to the acid, the latter in considerable excess, and not *vice versâ*, as in the last case the carbonic acid is likely to enter into combination with a portion of the magnesia as a bicarbonate, and thus escape the eyes of the manipulator. If the magnesia is heated after the carbonic acid and water are evolved, it soon loses its lightness and acquires a compact, lumpy form. By carefully observing these apparently trifling rules, a beautiful preparation will be obtained.

Properties.—Calcined magnesia forms a snow-white, impalpable, odourless, and tasteless powder, which at the ordinary red heat undergoes no change. Exposed to the air it quickly absorbs carbonic acid and water, becoming partially converted into basic carbonate of magnesia. Moistened turmeric paper is coloured brown by it. Water dissolves traces of it; on heating the aqueous solution it becomes turbid, but clears again on cooling. Dilute acids dissolve it quietly and readily; if gas bubbles are given off *carbonic acid* is present. If dilute sulphuric acid leaves a residue insoluble in water but dissolving when heated with solution of caustic potash, the magnesia contains *silica;* if soluble in a large quantity of water it is sulphate of lime (gypsum) and the magnesia contained *lime.* If silica and lime are present, the latter is most readily detached by the addition of oxalate of ammonia to the neutral solution of the sulphate. If in a solution of the sulphate, ammonia causes a precipitate not dissolved by sal ammoniac, *alumina* is present; the magnesia will be partially precipitated,

but is again taken up by sal ammoniac (ammonia is evolved, and a readily-soluble double salt results). *Iron* gives rise to a violet or bluish black turbidness on the addition of tannin to a neutral solution of the sulphate. If pure water agitated with the preparation afterwards gives a turbidness with nitrate of baryta or silver, *sulphuric* or *hydrochloric acid* is present, arising from the sulphates and chlorides not having been well washed from the carbonate of magnesia.

MAGNESIUM OXIDATUM SULPHURICUM DEPURATUM.

Sal Amarus.—Magnesiæ Sulphas.—Sulphate of Magnesia.—Epsom Salts.

FORMULA: $MgO + SO_3 + 7HO$.

Preparation.—Commercial sulphate of magnesia is generally of sufficient purity; when, however, this is not the case, as, for instance it becomes moist when exposed to the air, or appears coloured, it is dissolved in twice its weight of pure water with the application of heat, and filtered into a porcelain or stone vessel, in which it is allowed to rest for 1 or 2 days in a cool place. The crystals are then removed from the solution, and the latter evaporated to half; and the same repeated so long as pure crystals separate. The mother liquor is thrown away, the crystals are spread on paper, and dried in the air in a cool place.

Recapitulation.—Any deliquescent salts, as chloride of magnesium or calcium, adhering to the commercial salt, from their ready solubility remain in the mother liquor together with any colouring matter.

Properties.—Sulphate of magnesia crystallizes in rectangular and rhombic prisms and pyramids,

which in the commercial salt are so fine as to appear like needles; it is odourless, and of a bitter saline taste. In the air it is scarcely altered except in summer, when it slightly effloresces. When heated it fuses in its water of crystallization, then dries, and at a strong red heat becomes liquid again, without decomposing. It dissolves in 3 parts of water of the ordinary temperature, and in $1\frac{1}{3}$ when boiling; the solution has a neutral reaction. Alcohol does not dissolve it. Sulphate of magnesia is in general contaminated with *chloride*, which in the dilute solution are readily detected by nitrate of silver. If the base of the chloride is *lime*, oxalate of ammonia then causes a precipitate. If *alumina* is present, the precipitate caused in the solution of sulphate of magnesia by ammonia will not be again dissolved by sal ammoniac; what remains dissolves readily in caustic potash. *Iron*, if present, gives a violet or bluish black precipitate with tannin, and *copper* a chocolate one with ferrocyanide of potassium or a blue solution with solution of ammonia. *Potash*, which is sometimes present as a double salt of potash and magnesia, is detected in a concentrated solution by tartaric acid, causing on agitation a crystalline precipitate. *Soda* (as Glauber's salt) is to be suspected when the salt readily effloresces in the air; on dissolving such a salt in hot water the sulphate of soda, together with sulphate of magnesia, crystallizes on cooling, and may be detected by the shape of the crystals. The sulphate of soda is, however, detected with the greatest certainty, even in small quantities, by drying a portion of the salt, to drive off the water of crystallization, then finely powdering, adding to it half its weight of finely-powdered charcoal and exposing the mixture before the blowpipe, or in large quantities in a small covered crucible in a furnace, to a strong red heat. A portion of the mass when cool is laid on a piece of clean silver, and moistened with 1 or 2 drops of

water; if this gives the silver a black colour soda is present. Another portion is supersaturated in a narrow cylindrical glass with dilute sulphuric acid; if it evolves an odour of sulphuretted hydrogen, or changes a piece of filtering paper saturated with solution of acetate of lead of a black colour when held in the empty part of the glass, the presence of soda is equally certain. When sulphate of magnesia containing sulphate of soda is heated with charcoal to redness, only the latter is reduced, forming sulphuret of sodium, which in contact with silver forms sulphuret of silver, and treated with dilute sulphuric acid evolves sulphuretted hydrogen, by which the acetate of lead is changed to sulphuret. Of course these effects are produced if potash instead of soda is present; in order to determine whether potash is also present the mass, after heating to redness with charcoal, is treated with alcohol, filtered, the filtrate, evaporated to dryness, treated with hydrochloric acid, and a portion fused on a platinum wire before the blowpipe; if the outer flame is of an intense yellow colour soda is present. Alcohol dissolves the sulphurets, leaving the sulphate of magnesia and carbon; hydrochloric acid converts the sulphurets into chlorides, and these, even if much potash and but little soda be present, give before the blowpipe the reaction of the latter metal only; the remainder of the salt may then be tested for potash by chloride of platinum.

The method of testing the sulphate of magnesia for sulphate of soda, strongly recommended by Duflos, consists in triturating the salt with water and carbonate of baryta, and testing the mass with turmeric paper, which will be rendered brown only if the latter impurity be present; this method will be found to be inaccurate, for pure sulphate of magnesia treated in the same manner also acquires an alkaline reaction. The baryta abstracts the acid from the sulphate of magnesia, forming insoluble

sulphate of baryta and carbonate of magnesia. But the (neutral) carbonate of magnesia has the peculiarity of separating, at the moment of its formation, into insoluble basic carbonate (the ordinary magnesia alba), and readily-soluble bicarbonate, which latter possesses a strongly alkaline reaction :—

5 at. $MgO + CO_2$ and 4 at. HO, form
1 at. $3(MgO + CO_2 + HO) + (MgO + HO)$, and
1 at. $MgO + 2CO_2$.

MANGANUM CHLORATUM.

Manganesii Chloridum.—Protochloride of Manganese.

FORMULA : $MnCl + 4HO$.

Preparation.—In the preparation of chlorine from peroxide of manganese and hydrochloric acid, the chloride of manganese is obtained in such considerable quantities as to make it seldom necessary specially to prepare it. When it is intended to make use of the residue, oxide of manganese as free as possible from carbonates is chosen. But in order to obtain it quite pure, it is necessary to subject it to a special treatment. The residue from the formation of chlorine is filtered, diluted with water, and $\frac{1}{8}$ of it precipitated with carbonate of soda ; the precipitate is well washed by decantation, added to the other $\frac{7}{8}$ of the filtrate, and digested for some days with a gentle heat in a glass flask. If a filtered portion of it now imparts a violet or blue colour to a solution of tannin, another portion must be precipitated, and the same treatment pursued. When tannin has no further action, a small portion of it is rendered slightly acid with hydrochloric acid, and sulphuretted hydrogen gas passed through it; if this causes any precipitate the whole of the filtrate is treated similarly, the precipitate separated by filtration, and the clear liquid evaporated to crystallization. The crystals are dried between filtering paper,

and kept in a well-closed bottle. The very last portion of mother liquor may be thrown away.

When the chloride of manganese is required for a purpose in which a small portion of lime or magnesia is of no consequence, the solution, after treating with carbonate of manganese, may be at once evaporated to dryness in a sand bath.

Recapitulation.—The formation of chloride of manganese, on treating peroxide with hydrochloric acid, has already been explained under the article "CHLORUM AQUOSUM." The purest manganese must be chosen, as much of it contains a considerable amount of carbonate of lime which dissolves and prevents a quantity of the manganese salt from crystallizing. By filtering the liquor after the generation of the chlorine, any excess of peroxide of manganese is removed. On precipitating a portion of the liquor with carbonate of soda, the insoluble carbonate of manganese is thrown down (as a hydrate) in white flakes, whilst the chloride of sodium remains dissolved :—

1 at. MnCl., 1 at. $NaO + CO_2$, and 1 at. HO, form
1 at. $MnO + CO_2 + HO$, and 1 at. NaCl.

The latter is removed by washing. On returning this precipitate to the remainder of the manganese solution, the protoxide of manganese displaces the iron existing as chloride, (and allways found in black oxides of manganese,) taking up its chlorine and giving it oxygen; the chloride of manganese remains dissolved, the oxide of iron precipitating as a brown flocculent hydrate, with which the carbonic acid cannot combine, and therefore is evolved :—

3 at. $MnO + CO_2 + HO$, and 1 at. Fe_2Cl_3, form
3 at. MnCl, 1 at. $Fe_2O_3 + 3HO$, and 3 at. CO_2.

In the same manner any alumina that may be

present in the solution will be evolved. This change does not take place at once, but gradually; it is effected more readily in the warm. With tannin we determine whether iron is present or not, and this reagent is the more satisfactory, causing no change in the manganese. When the quantity of iron is very considerable, it is necessary to subject the solution to a second treatment with carbonate. If it contain copper or chloride of lead, they are removed by the treatment with sulphuretted hydrogen. By evaporation the purified solution is obtained crystallized. After two or three crystallizations a mother liquor remains containing the other impurities, as the chlorides of calcium and magnesium, which may be thrown away as worthless.

Properties.—Chloride of manganese forms pale rose-coloured tabular clear crystals, odourless and of a bitter astringent taste. In the air they slowly attract moisture and deliquesce. When warmed, they give up a portion of their water of crystallization without entirely fusing; with a stronger heat the remainder of the water is given off, and the salt liquifies; if the heat is sudden a portion of the chlorine (water being decomposed) is given off as hydrochloric acid. When all the water is given off, the whole of the chlorine at a red heat is gradually evolved, and there remains an oxide $= MnO + Mn_2O_3$. In the decomposition of the water the oxygen passes to the manganese, the remainder of the latter which gives off its chlorine uncombined is oxidized at the expense of the atmospheric air. Water and alcohol readily dissolve this salt, forming neutral solutions. If it contains *iron*, the tannin will form a violet or blue turbidness of tannate of iron. When the solution acidified with hydrochloric acid, gives a black precipitate with sulphuretted hydrogen *lead* or *copper* is present; if lead, sulphuric acid will cause a white precipitate, and copper will yield a blue solution with ammonia. *Alumina* is detected by

boiling the salt with excess of liquor potassæ, and on shaking the solution with sal ammoniac will cause a white turbidity. The potash throws down the manganese and alumina, both as white hydrates, but in excess it again dissolves the alumina, leaving the hydrated protoxide of manganese, which from the oxygen of the air is partly converted into a brown hydrated oxide. When sal ammoniac is added to the filtered solution chloride of potassium is formed and ammonia evolved, in which alumina, being insoluble, precipitates. Previously to testing for alumina any lead that is present must be thrown down with sulphuretted hydrogen, the oxide of this metal being also soluble in potash solution, and precipitated by sal ammoniac.

To discover *lime* and *magnesia* the solution is treated with excess of hydrosulphuret of ammonia, when the manganese is thrown down as a flesh-coloured sulphuret, the iron, copper, and lead as black sulphurets, and the alumina as a white hydrate; filter, add to the filtrate oxalate of ammonia in excess, filter off the oxalate of lime, and add phosphate of ammonia, when the magnesia precipitates as fine white granular crystals; (*vide* AMMON. CHLORAT.). *Sulphates* are tested for with chloride of barium.

MANGANUM CARBONICUM.

Manganesii Carbonas.—Carbonate of Protoxide of Manganese.

FORMULA: $MnO + CO_2 + HO$.

Preparation.—1 Part of crystallized chloride of manganese is dissolved in 12 parts of pure water, and a solution of carbonate of soda added so long as it causes a precipitate; $1\frac{1}{2}$ parts of crystallized soda will suffice. The precipitate is collected on a filter, exhausted with water, and dried in a gentle heat.

Recapitulation.—Chloride of manganese and carbonate of soda are mutually decomposed, forming carbonate of protoxide of manganese and chloride of sodium :—

1 at. $MnCl + 4HO$, and 1 at. $NaO + CO_2 + 10HO$, form
1 at. $MnO + CO_2 + HO$, 1 at. NaCl, and 13 at. HO.

1238 Parts of crystallized chloride of manganese require 1790 parts of crystallized carbonate of soda. The precipitate at first a pure white becomes during its exhaustion with water, and still more on drying, of a yellowish-gray colour, from the action of the atmospheric oxygen which forms with it a higher oxide ; in a quantitative point of view this change is so inconsiderable as to equal scarcely $\frac{1}{100}$ of the preparation.

Properties.—The carbonate of manganese freshly precipitated is a snow-white powder, but that which has been dried in the air has a grayish-yellow tint, and contains about $\frac{1}{100}$ of its weight of oxide of manganese. It has neither taste nor odour. When heated it gives off water and carbonic acid, leaving pure protoxide of manganese, that is, if the air be entirely excluded, otherwise by attracting oxygen the protoxide becomes converted into a blackish-brown sesquioxide :—

3 at. MnO, and 1 at. O, form
1 at. $MnO + Mn_2O_3$.

The residue on heating may by the admission of the air be converted into a compound, resembling minium in composition, of 2 at. protoxide and 1 at. peroxide of manganese $= 2MnO + MnO_2$: which like minium is separated by nitric acid into soluble protoxide and insoluble peroxide. Water has no action on proto-carbonate of manganese; acetic acid dissolves it in the heat to a pale rose-coloured solu-

tion, carbonic acid being evolved ,and the brownish-black oxide of manganese* forming a residue. Nitric and hydrochloric acids dissolve it entirely in the cold; with the latter a little free chlorine is eliminated on account of a small quantity of oxide present:—

1 at. Mn_2O_3, and 3 at. HCl, form
2 at. MnCl, 3 at. HO, and 1 at. Cl.

Other impurities as *iron, copper, lead, alumina, lime, &c.*, are to be detected in the solution of the neutral chloride as with the previous one.

MORPHINUM PURUM.

Pure Morphine or Morphium.

FORMULA: $C_{34}H_{18}NO_6 + 2HO = \overset{+}{M}o + 2HO$.

Preparation.—After trying several of the methods which appeared to me most advantageous, I can recommend that of Mohr's as the best, according to my experience. 20 Parts of good (so-called Smyrna) opium is cut into slices and boiled, in a copper or leaden vessel, with 60 parts of water, being constantly stirred with a wooden spatula, for ½ an hour, or until all the slices are entirely softened, strain through a pointed bag of rather coarse linen, press the residue, and treat it twice with fresh water in the same way. The strained liquor is evaporated in the same vessel to half its bulk; 40 parts of water, containing 5 parts of hydrate of lime, are then heated to boiling, and the condensed liquid gradually added to it; the whole is then boiled for a quarter of an hour, strained, pressed, and the residue twice boiled, each time

* Its entire solubility in nitric acid denotes that this is really an oxide (hydrated oxide), and not a mixture of proto- and peroxides.

with 50 parts of water. The mixed fluids containing lime are concentrated to 40 parts and filtered. The filtrate is heated in a porcelain dish to boiling, 2 parts of muriate of ammonia are added, and the whole allowed to stand in a warm place, with frequent stirring, one hour, or until an evident evolution of ammonia takes place, then removed to a cold one. After standing eight days the brown crystalline precipitate that has separated is collected on a strainer, the liquid which passes off evaporated to half, and this again allowed to stand eight days in a cool place, strained, pressed, the mother liquor thrown away, and the two residues mixed. To the two precipitates, after washing them with cold water, so much water is added that the whole weighs about 20 parts, then add pure hydrochloric acid until the liquid acquires a feebly acid reaction; it is now heated to boiling, filtered whilst hot, and evaporated to a small bulk. After it has stood some days, the crystalline mass which forms is collected on linen, strongly pressed, again evaporated and strained: this last black mother liquor may be kept for mixing with the opium at another preparation of morphine. The crystallized and dried mass is dissolved in four times its weight of boiling water, and the solution added to a boiling mixture of 3 parts hydrate of lime and 24 parts water; the straining, washing, treating with sal ammoniac ($1\frac{1}{2}$ parts) and hydrochloric acid are repeated as before, the precipitate dissolved in 30 times its weight of hot water, and the solution, if coloured, treated with freshly heated wood charcoal; when cold it is precipitated with ammonia, of which too large an excess must be avoided. The precipitated white crystalline needles are collected on a filter, rinsed with cold water, and dried with a gentle heat. The product will be $\frac{1}{10}$ or $\frac{1}{12}$ of the weight of opium used.

The precipitate which ammonia causes in the pre-

paration of meconic acid is dissolved in dilute hydrochloric acid, and treated exactly like the watery solution of opium.

Recapitulation.—The morphine (together with the small quantities of narcotine, codeine, thebaine, &c.) are combined in opium with meconic (and sulphuric) acid. Water dissolves the salts of morphine, codeine, thebaine, and (the greater portion of) narcotine; the codeine and thebaine, on account of the little contained, can only be isolated when operating on large quantities of opium. When the watery solution comes in contact with the boiling milk of lime, the acids pass to the lime, forming meconate and sulphate of lime, the alkaloids precipitate, but the morphine redissolves in the lime water, the others remaining in the residue, from which narcotine, codeine, and thebaine may be extracted with alcohol or ether. For convenience' sake the lime solution is evaporated, and during this process, from the access of the carbonic acid in the atmosphere, a portion of the lime precipitates as carbonate, and with it the morphine that it had previously held in solution, this is only trifling, yet quite sufficient to repay (when a good quantity has been collected) for its exhaustion with alcohol. When sal ammoniac is added to the condensed and filtered solution, both compounds are decomposed; the oxygen of the lime forms water with one atom of hydrogen of the ammonium, the calcium combining with the chlorine, ammonia is evolved, and the morphine, robbed of its solvent, precipitates with some colouring matter. In order to ensure entire decomposition heat must be employed, and afterwards the whole is allowed quietly to rest for several days. The mother liquor, when further evaporated, yields a little more morphine. The quantity of sal ammoniac mentioned is more than sufficient to throw down all the morphine, but the excess is of no ill consequence, and insures entire precipitation. In

order to purify this morphine further from colouring matter, it must be combined with some acid with which it forms a readily-crystallizable and not very soluble salt; for this purpose hydrochloric answers best. Most of the colouring matter, with a little hydrochlorate of morphine, remains in the mother liquor, and what still adheres to the salt will be entirely removed by the second treatment with lime, etc. The muriate of morphine obtained the second time forms with water, only a slightly coloured solution, which is rendered perfectly colourless by shaking with freshly-prepared charcoal, and on the addition of caustic ammonia precipitates as fine white needles, of a silky lustre. An excess of ammonia is to be avoided, as the morphine will be redissolved by it. If wished for in large crystals, it is dissolved in strong alcohol, and the solution slowly evaporated. It is sometimes possible to decolourize the first muriate of morphine entirely with charcoal, and thus render the treatment with lime unnecessary: it is well to try this with a small portion first.

The precipitate obtained by evaporating the morphine and lime solution (*vide supra*) is dried, exhausted with strong alcohol, the solution concentrated, taken up with hydrochloric acid, and the salt either purified alone or used up with a fresh precipitate from opium.

Properties.—Pure morphine forms fine white needles, of a silky lustre, and, if obtained from an alcoholic solution, by slow evaporation, in tolerably large, colourless, semi-transparent, four-sided prisms. It is odourless and tastes slightly bitter. It undergoes no change in the atmosphere. Carefully heated it gives off water, fusing to a yellow liquid, which still more strongly heated decomposes, burning and leaving a carbonaceous residue, which heated long enough must be entirely consumed. Water dissolves but a trace of morphine (about $\frac{1}{1050}$), but acquires a bitter

taste from it. Alcohol of 80 per ct. dissolves, at the ordinary temperature, $\frac{1}{30}$, boiling $\frac{1}{20}$ its weight of morphine; the solution has a positive alkaline reaction. In ether it is insoluble. Dilute acetic, hydrochloric, nitric, and sulphuric acids dissolve it with the greatest readiness, and are neutralized by it entirely; their solutions, as well as the alcoholic, have an intensely bitter taste. Tincture of galls gives, with neutral solutions, a dirty white turbidness; the slightest excess of acid dissolves the precipitate (tannate of morphine). Persalts of iron give, with salts of morphine, a deep blue colour which is dissipated by heating. The reason of this behaviour has not been explained, nor has that with solution of iodic acid, from which, when rubbed with morphine, the iodine is liberated. Solution of caustic potash or soda, as well as caustic baryta, strontia, and lime readily dissolve morphine. This property of morphine allows its purity to be readily judged of. If, on shaking with ether and evaporating, a crystalline residue is left, it is contaminated with *narcotine;* and this base is also present if an acid solution of morphia is rendered turbid by tincture of galls, as well as if a portion insoluble in caustic potash solution dissolves in alcohol and ether. When alcohol does not entirely dissolve the preparation, the residue is generally a mineral substance, *phosphate of lime*, *gypsum*, *carbonate of lime*, &c.; if it gives, on burning, an empyreumatic odour, it probably contains some vegetable powder. The nitric acid or dilute acetic acid solution must give no precipitate with nitrate of silver, nitrate of baryta, oxalate of ammonia, or phosphate of ammonia, which denote the presence of *hydrochloric* and *sulphuric acids*, *lime*, and *magnesia*. If oxalate of ammonia gives a precipitate it must be removed previously to testing for magnesia.

MORPHINUM ACETICUM.

Acetate of Morphine.

+

FORMULA: $\overline{Mo} + \overline{A} + 6HO$.

Preparation.—2 Parts of pure Morphine are intimately mixed with 2 parts of water in a mortar, warmed in a sand bath, and concentrated acetic acid added to it until dissolved; 1 part of acid, spec. grav. 1·045, will be sufficient. The solution is poured on a shallow porcelain plate, and dried at a temperature not exceeding 120 Fah., powdered and preserved in a closed vessel in a cool place. The yield will be about $\frac{1}{8}$ more than the weight of the morphine employed.

Recapitulation.—Morphine is readily dissolved and neutralized by acetic acid:—

1 at. $C_{34}H_{18}NO_6 + 2HO$, 1 at. $C_4H_3O_3$, and 4 at. HO, form

1 at. $\overline{Mo} + \overline{A} + 6HO$.

3775 Parts of crystallized morphine require 638 parts of anhydrous, or 1772 parts of acetic acid, spec. grav. 1·045, (=64 per ct. water). The salt crystallizes with difficulty, the solution is therefore evaporated to dryness, which, to avoid decomposition (the volatilization of any of the constitutional acid of the salt) must be done at a moderate temperature.

Properties.—Acetate of morphine forms a white, or nearly white, fine crystalline powder, which has a feeble smell of acetic acid, and bitter taste. It is unalterable in the air at the ordinary temperature. Gently heated it loses a portion of its acid, heated more strongly it fuses, decomposes, and burns without residue. It is soluble in 17 parts of cold and equal parts of hot water; by cold alcohol of 80 per

ct., only $\frac{1}{14}$ is taken up, but boiling alcohol dissolves as much as boiling water; the solutions have a feeble acid reaction. If water leaves a residue, readily soluble in alcohol, the salt has lost a portion of its acid. To test for impurities and adulteration, refer to the preceeding article.

MORPHINUM MURIATICUM.

Hydrochlorate of Morphine.

+

FORMULA: Mo + HCl + 6HO.

Preparation.—The hydrochlorate of morphine may be obtained in making the pure morphine. To prepare it from pure morphine, 2 parts of the latter are rubbed in a porcelain dish with 5 parts of water, heated to boiling, and pure hydrochloric acid added until entirely dissolved (1 part of acid, spec. grav. 1·130, will suffice), and allowed to cool. After standing a day, the crystals which form are separated from the supernatant liquid, which is evaporated to further crystallization. The salt is spread out and dried on filtering paper. Its weight should be $2\frac{1}{2}$ parts.

Recapitulation.—As under Acetate of Morphine. 3775 Parts of crystallized morphine require 455 parts of anhydrous, or 1750 parts of hydrochloric acid, of spec. grav. 1·130 (=74 per ct. water). As the salt is somewhat difficultly soluble in cold water, a large portion of it may be at once separated when but little hot water is employed to dissolve it.

Properties.—Hydrochlorate of morphine forms white feathery, indistinct, crystalline needles, odourless, and of a strongly bitter taste. It is unalterable in the air; heated it fuses, loses its water, decomposes, and burns without residue. 1 Part of the salt is soluble in 22 parts of water at the ordi-

nary temperature, and in less than its weight of boiling water; nevertheless, alcohol of 80 per ct. dissolves only $\frac{1}{50}$ cold, and $\frac{1}{10}$ its weight when hot; the solutions have a neutral reaction. The tests for impurities, &c., are as under MORPHINUM PURUM.

MORPHINUM SULPHURICUM.

Sulphate of Morphine.

$$\overset{+}{\text{Mo}} + \text{SO}_3 + 6\text{HO}.$$

FORMULA: $\overset{+}{\text{Mo}} + \text{SO}_3 + 6\text{HO}$.

Prepared as the preceding. 3775 Parts of Morphine require 613 parts of hydrated sulphuric acid, or 3678 parts of dilute acid containing $\frac{1}{8}$ of the mono-hydrated acid. In its properties it most nearly resembles the hydrochlorate, but dissolves in water and alcohol very readily.

NATRIUM.

Sodium.

FORMULA: Na.

Preparation.—2 Parts of crystallized carbonate of soda are dissolved in a capacious iron pot, in 2 parts of hot water, and powdered tartaric acid added so long as effervesence is caused by it; (one part will suffice). It is then evaporated to dryness, and the dried salt carbonized in a covered iron crucible. 20 Parts of the charred salt are well mixed with 3 parts of finely-powdered and 6 parts of coarsely-powdered wood charcoal, placed in a wrought-iron mercury bottle, and the same process followed as given under the article KALIUM. 20 Parts of the charred soda salt yield from 3 to 4 parts sodium.

Recapitulation.—By saturating carbonate of soda

with tartaric acid, carbonic acid is given off, and neutral tartrate of soda formed :—

1 at. $NaO + CO_2 + 10HO$, and 1 at. $\overline{T} + HO$, form 1 at. $NaO + T$, 1 at. CO_2, and 11 at. HO.

1790 Parts of crystallized carbonate of soda require 938 parts of crystallized tartaric acid. By heating to low redness, we obtain, similarly to tartrate of potash, an intimate mixture of carbonate of soda and carbon. The acetate of soda is generally used, but I prefer the tartrate, as yielding a product richer in carbon. On account of the greater fusibility of the carbonate of soda, more charcoal is mixed with it than with the carbonate of potash. The process of the reduction of the sodium agrees in every respect with that of potassium.

Properties..—Sodium is met with in soft globules of a silvery whiteness, otherwise resembling potassium in external appearance, having a spec. grav. 0·96, and fusing at 190° Fah. In the air it is not so readily oxidized as the potassium, but cold water is decomposed by it with greater violence, yet without inflaming; which only occurs when warmed. The colour of the flame is a deep yellow. In coal or mineral naptha it preserves its metallic lustre longer than potassium (*vide* KALIUM).

NATRIUM CHLORATUM DEPURATUM.

Sodii Chloridum.—Purified Chloride of Sodium.

FORMULA : NaCl.

Preparation.—80 Parts of commercial (common) salt are dissolved in a glass or porcelain dish with 180 parts of water, and 1 part of hydrate of lime added ; the whole is allowed to remain, with frequent stirring, for one week, at the ordinary tem-

perature, and, when filtered, the filtrate is treated with solution of chloride of barium as long as necessary (about 2 parts will be required), filtered, when the precipitate has thoroughly subsided, and crystallized carbonate of soda (3 to 3¾ parts) added to the clear liquid. After the precipitate has deposited, it is filtered, the clear liquid neutralized with pure hydrochloric acid, and evaporated to dryness in a porcelain dish. The salt will equal 70 to 75 parts, it must be kept in a closed bottle.

Recapitulation.—The most common impurities in commercial chloride of sodium are:—iron (as chloride), magnesia (as chloride of magnesium), lime (as chloride of calcium), and sulphuric acid, as sulphate of soda. By crystallization, these are but imperfectly separated, the chloride of sodium, like nitre, having the property of enclosing a portion of the mother liquor in their interstices. The method of purification above described, insures the removal of all impurities without the fear of any additional ones. The lime being a stronger base, throws down the iron and magnesia, exchanging with them its oxygen for chlorine, and forming a readily soluble chloride of calcium; in order to insure their entire decomposition, the lime must be in excess, which gives the solution a strong alkaline reaction. The sulphuric acid is then precipitated by chloride of barium, and the sulphate of baryta is allowed thoroughly to precipitate, otherwise it would pass through the filter. The lime and excess of chloride of barium, are thrown down as insoluble carbonates by carbonate of soda; this precipitate must not be filtered off for several days, by which time it is entirely deposited, and yields a clear filtrate. The excess of carbonate of soda is converted by the hydrochloric acid into chloride of sodium, and any excess of the acid is volatilized during the evaporation to dryness.

Carbonate of ammonia is sometimes substituted

for the carbonate of soda, to throw down the lime and baryta; it possesses, however, two evils; the latter base is not so thoroughly precipitated by it as by carbonate of soda, for the sal ammoniac formed dissolves a small portion of the precipitate; and secondly it is necessary to heat the salt to redness to remove the sal ammoniac.

Properties.—Salt thus purified forms a snow-white crystalline powder consisting of exceedingly fine cubes, odourless, and having a peculiar saline taste. It undergoes no change in the air; at a red heat it fuses and gradually volatilizes without decomposition. Water of all temperatures between the freezing and boiling dissolves it equally; 1 part of water dissolves 0·37 parts or 1 part is soluble in 2·7 of water, the solution has a neutral reaction, cold alcohol of 80 per ct. dissolves $\frac{1}{200}$ boiling, $\frac{1}{85}$ of salt. If it absorbs moisture from the air, it contains deliquescent salts as *chloride of calcium* or *magnesium*. A turbidness caused in the aqueous solution by oxalate of ammonia indicates *lime*, and if on the separation of this precipitate, phosphate of ammonia instantly or after some little time gives another precipitate it is from *magnesia* (*vide* AMMON. CHLORATUM). Tannin or ferrocyanide of potassium gives it, if *iron* be present, a violet or dark blue colour; and chloride of barium a white precipitate, should it contain *sulphuric acid*.

NATRIUM OXIDATUM LIQUIDUM.

Liquor Sodæ.—Solution of Caustic Soda.

FORMULA: $NaO + xHO$.

Preparation.—2 Parts of crystallized carbonate of soda are dissolved in a silver or clear iron vessel with 16 parts of boiling water; and, constantly stirring with a bright iron or silver spatula; 1 part

of hydrate of lime is added, then boiled for ¼ of an hour and filtering, a small filtered portion is tested with dilute sulphuric acid; should this cause the formation of a gas bubble lime must still be added. If the two mix quietly as is generally the case, the liquid and residue are both thrown on a conical strainer suspended in a convenient jar, and the liquid returned to the filter until it passes off clear; it must then be preserved in a glass stoppered bottle. The mass remaining in the strainer is then returned to the iron pot, diluted with 12 parts of water, warmed and again strained. The iron pot is now cleaned, the first portion of the liquor returned to it and boiled, the second being added as fast as it strains; the whole must be boiled as rapidly as possible until a small portion withdrawn from it and cooled possesses a spec. grav. 1·333. The pot is now removed from the fire, the contents still warm are poured into a glass stoppered bottle, the spec. grav. again taken and if necessary reduced with water to 1·333. The product will be 1⅔ parts.

To obtain dry caustic soda proceed as with caustic potash.

Recapitulation.—Carbonate of soda yields its acid to the lime, which becomes converted into insoluble carbonate of lime:—

1 at. $NaO + CO_2$ and 1 at. CaO, form
1 at. NaO and 1 at. $CaO + CO_2$.

1790 Parts of crystallized carbonate of soda (which contains 10 at. water) require 463 parts of hydrate of lime; but for the reasons detailed under the article Kalium Oxyd. Hydrat. more lime must be taken; the other explanations are the same in both articles.

Properties.—Caustic solution of soda of spec. grav. 1·333 contains 24 per ct. soda, and 76 per ct. or 11 at. water. In its physical and chemical rela-

tions it agrees with caustic potash so nearly, that it is needless to recapitulate them. It is, however, free from turbidness on the addition of tartaric acid in excess, which causes a precipitate with potash.

NATRIUM OXIDATUM ACETICUM.

Sodæ Acetas.—Acetate of Soda.

FORMULA: $NaO + \bar{A} + 6HO$.

Preparation.—(a) With Acetic acid. A convenient quantity of pure acetic acid is poured into a beaker glass, and, constantly stirring, powdered crystals of carbonate of soda added as long as it causes an effervescence, or until the acid reaction is removed. To 1 part of acid spec. grav. 1·045, about 1 part of soda will be requisite. The acid reaction is now restored by a little acetic acid, the solution filtered if necessary, evaporated to half and placed in a cool spot to crystallize. The crystals which separate are after some days thrown on a filter, the mother liquor is treated with a little acetic acid, if it has lost its acid reaction, again evaporated, and this repeated as long as crystals form. The whole of the salt is spread out on filtering paper and dried at the ordinary temperature or with a very gentle heat; and must be kept in a cool place. The yield will be $\frac{7}{8}$ the weight of the soda employed.

(b) With Acetate of Lead. A solution of 1 part of acetate of lead in 6 parts of distilled water is precipitated with 1 part of carbonate of soda in 3 parts of water (for 4 parts of acetate of lead about 3 parts of carbonate of soda); after subsiding, it is filtered, the precipitate washed with water, the filtrate treated with a little sulphuretted hydrogen, sufficient to make the odour of this gas perceptible, evaporated to about the weight of the sugar of lead

employed, supersaturated with acetic acid and allowed to crystallize. From 4 parts of acetate of lead about $2\frac{1}{2}$ parts of acetate of soda are obtained.

Recapitulation.—(*a*) Acetic acid drives off the carbonic acid and forms with the soda acetate of soda:—

$$1 \text{ at. } NaO + CO_2 \text{ and } 1 \text{ at. } \bar{A}, \text{ form}$$
$$1 \text{ at. } NaO + \bar{A} \text{ and } 1 \text{ at. } Co_2.$$

1772 Parts of acetic acid, spec. grav. 1·045 (containing 36 per ct. pure acid) are saturated by 1790 parts of carbonate of soda.

To save fuel the strongest commercial acid should be employed. The salt dried in the warm is anhydrous.

(*b*) Sugar of lead (neutral acetate of lead) and carbonate of soda become mutually converted into insoluble carbonate of lead and readily soluble acetate of soda:—

$$1 \text{ at. } PbO + \bar{A} + 3HO \text{ and } 1 \text{ at. } NaO + CO_2 + 10HO, \text{ form}$$
$$1 \text{ at. } PbO + CO_2, \ 1 \text{ at. } NaO + \bar{A}, \text{ and } 13 \text{ at. } HO.$$

2370 Parts of sugar of lead require 1790 parts of crystallized carbonate of soda entirely to decompose them; but a slight excess of the latter is necessary to insure that all the lead salt is decomposed. To remove the last traces of lead remaining in the solution, sulphuretted hydrogen is passed through it, and to neutralize the free soda acetic acid is added. The precipitate is saved as carbonate of lead.

Properties.—Acetate of soda crystallizes in tolerably large fluted oblique rhombic prisms, which have a faint odour of acetic acid and a pungent saline taste. In the air, and still more readily in warm air, it effloresces, giving off water. Heated more strongly it fuses in its water of crystallization, then solidifies, again fuses and finally gives off its acetic

acid like acetate of potash. 1 Part of the salt dissolves in $2\frac{1}{2}$ parts of water at the ordinary temperature, whilst its own weight of boiling water is sufficient; in alcohol it is readily soluble. The solutions must possess a neutral or only feeble acid reaction. The adulterations and impurities are such as are noticed under acetate of potash.

NATRIUM OXIDATUM BICARBONICUM.

Sodæ Bicarbonas.—Bicarbonate of Soda.

FORMULA: $(NaO + CO_2) + (HO + CO_2.)$

Preparation.—Carbonate of soda is formed in the same manner as bicarbonate of potash; but being generally required in the state of powder it is more advantageous to prepare it by the dry method. The crystallized soda (containing 10 at. of water) is not applicable for this purpose, for on its conversion into bicarbonate (which contains only 1 at. water) the whole mass becomes dissolved by the 9 at. of water in excess. For this purpose carbonate of soda which has effloresced in the air without heat being applied, is, on account of its lightness and porosity, to be preferred; it generally contains 3 at. of water.

If the opportunity occurs of employing carbonic acid from fermenting liquids, the effloresced soda is placed about 2 inches deep on a linen strainer near the vessels, and the process conducted as under KALIUM OXIDAT. BICARBON.

The apparatus employed in the preparation just mentioned is also applicable in the present one. In this case the limb of the tube (*e*) which dips into the bottle (*f*) is as wide as possible, the end covered with a piece of linen and conducted nearly to the bottom of the bottle; through the other opening of

the bottle, which is afterwards closed with a bladder, sufficient effloresced soda is poured nearly to fill it, the carbonic acid is then generated, &c., &c.

Whichever way it is prepared the saline mass is rubbed to a fine powder, and spread out in the air until it appears quite dry; it should be kept in closed vessels.

If the soda employed contains other salts (generally chloride of sodium or sulphate of soda) the bicarbonate is of course not free from them; it may however be freed from them with trifling loss by simply washing with *cold water*. The process is the same as that given under KALI NITR. The salt is powdered as finely as possible, $\frac{2}{3}$ its weight of pure water added, the paste thrown into the apparatus and water gradually added as long as the liquid which escapes gives, when neutralized with nitric acid, a precipitate on the addition of nitrate of baryta or silver. The pasty mass spread on a shallow dish is dried in the air. Commercial bicarbonate can be similarly purified and any simple carbonate it may contain will at the same time be removed.

Recapitulation.—As under bicarbonate of potash. The effloresced soda containing 3 at. of water is entirely saturated by carbonic acid without dissolving, one of the atoms of water combines with it chemically, the other two remain in admixture, causing the salt to agglutinate, but are given off on exposure to the air. The linen tied over the end of the tube allows the gas to pass through without the possibility of the tube becoming choked. The chlorides, sulphates, and simple carbonate of soda being much more soluble than the bicarbonate are removed by washing.

The wash-water is evaporated to dryness, when all the bicarbonate is changed to carbonate of soda. The residue may be employed in cases where chloride of sodium and sulphate of soda are not detrimental.

Properties.—Bicarbonate of soda forms a snow-white odourless powder of a mild very slightly caustic taste, it dissolves in 13 parts of cold water; in other respects it resembles bicarbonate of potash; the tests are also similar.

NATRIUM OXIDATUM CHLORICUM.

Sodæ Chloras.—Chlorate of Soda.

FORMULA: $NaO + ClO_5$.

Preparation.—3 Parts of crystallized sulphate of ammonia and 5 parts of chlorate of potash are dissolved in a porcelain dish with 15 parts of hot water; the solution is evaporated in a water-bath, with constant stirring, to the consistence of a thin paste, this on cooling is put into a capacious glass flask, supersaturated with four times its weight of alcohol of 80 per ct., digested for one day at a gentle heat, filtered, and the residual saline mass washed with alcohol. To the mixed alcoholic solutions is added one fourth their weight of water, the alcohol is distilled off in a retort, the solution poured into a porcelain dish, then diluted with its weight of water and 5 parts of powdered crystallized carbonate of soda are added; the mixture is now heated, with constant stirring, in a water bath, as long as the smell of ammonia is perceptible, and diluted with water if it becomes too thick whilst this is the case; finally it is evaporated to dryness. The salt is redissolved in twice its weight of hot water and set aside to crystallize; if after obtaining one or two crops of crystals the mother liquor has a powerful alkaline reaction, it may be set aside for a fresh preparation. The yield is rather more than the sulphate of ammonia employed.

Chlorate of soda cannot be prepared like the

chlorate of potash by treating its carbonate with chlorine because the chloride of sodium which is formed at the same time and in larger quantities than the chlorate of soda, possesses the same degree of solubility; neither will the separation of the two salts by means of alcohol, although frequently recommended, be found effectual. If, as in the method for the preparation of chlorate of potash 1 at. of chloride of sodium and 6 at. of lime, or 1 at. of carbonate of soda and 5 at. of lime are treated with chlorine, the chloric acid remains in combination with the lime, and the chloride of sodium whether previously present in the mixture or formed during the process, will crystallize out as such. It is therefore clear that the readiness with which chlorate of potash forms is due to its slight solubility, whilst the opposite quality is a great impediment in the preparation of chlorate of soda.

The method hitherto most frequently employed, consists in decomposing bitartrate of soda with chlorate of potash, filtering off the slightly soluble cream of tartar thus formed, evaporating the filtrate to dryness, treating with water and again crystallizing. By this convenient process a salt of a nice appearance is obtained, but which is contaminated with some bitartrate of potash as will be evident from its puffing up and blackening when heated.

By separating the potash from chlorate of potash by means of fluosilicic acid, and then neutralizing with soda, the preparation, like the last, will contain potash, and at the same time is more expensive than the one first given.

Recapitulation.—When sulphate of ammonia and chlorate of potash in aqueous solution are brought together, an exchange of elements ensues, and two soluble salts are again formed, chlorate of ammonia and sulphate of potash:—

1 at. $NH_4O + SO_3 + HO$ and 1 at. $KO + ClO_5$, form 1 at. $NH_4O + ClO_5$, 1 at. $KO + SO_3$, and 1 at. HO.

938 Parts of crystallized sulphate of ammonia require 1533 parts of chlorate of potash. These two salts are separated by alcohol, in which sulphate of potash is insoluble; previous to the addition of the alcohol most of the water must be evaporated, but not the whole of it, otherwise the chlorate of ammonia would decompose, partly volatilizing, partly changing into chloride of ammonium; the other volatile products which separate are water, chlorine, nitrous oxide, and oxygen :—

2 at. $NH_4O + ClO_5$, form
1 at. NH_4Cl, 4 at. HO, 1 at. Cl,
1 at. NO and 7 at. O.

Even in evaporating to the prescribed thickness a temperature higher than that obtained by a water bath must be carefully avoided. The decomposition of a certain portion of the chlorate of ammonia is unavoidable; this, however, will not be considerable if the previous rules are carefully observed. In order to reobtain the alcohol with which the pasty mass is treated, water is added and the whole distilled; the residual aqueous solution of chlorate of ammonia (which for fear of decomposition must not be further evaporated) is decomposed, after the necessary dilution, by carbonate of soda at a gentle heat, into chlorate of soda, and carbonate of ammonia which volatilizes :—

1 at. $NH_4O + ClO_5$ and 1 at. $NaO + CO_2$, form
1 at. $NaO + ClO_5$ and 1 at. $NH_4O + CO_2$.

The chlorate of ammonia obtained from 938 parts of crystallized sulphate of ammonia and 1533 parts of chlorate of potash, will require 1790 parts of crystallized carbonate of soda. On account of the trifling decomposition of the chlorate of ammonia which always occurs, rather less than the stochiometrical proportion of soda must be used, in order to prevent any free carbonate of soda from remain-

ing mixed with it; 3 parts of sulphate of ammonia and only 5 of carbonate of soda. The exchange of elements between the chlorate of ammonia and carbonate of soda only takes place gradually, and during its occurrence the smell of the carbonate of ammonia evolved is perceptible; in order to remove the latter entirely, it is evaporated to dryness. The re-solution and crystallization is unnecessary, unless the salt is required in a crystalline form, as both the crystallized and uncrystallized salts are anhydrous. If, however, from want of sufficient care in the preparation, a large portion of chlorate of ammonia is decomposed and lost, the whole of the carbonate of soda will not be converted into chlorate, but portions of it will remain mixed with the latter salt, and in this case re-crystallization of the salt is necessary, when the carbonate of soda, with a little chlorate of soda and chloride of sodium (which is formed by the spontaneous decomposition of chlorate of ammonia by heat into chloride of ammonium) remain in the mother liquor.

The alcohol after the distillation generally possesses a feeble smell of chloric ether and an acid reaction (from the decomposition of a certain portion of the chlorate of ammonia during the distillation and the action of the liberated chlorine); it is, however, applicable to many purposes, as the manufacture of spiritus salis dulcis, &c.

Properties.—Chlorate of soda forms colourless rhombohedric crystals, which are odourless and of a mild saline cooling taste. In the air it remains unaltered; heated it fuses, evolves oxygen, and finally becomes entirely converted into chloride of sodium (*vide* KALI CHLORICUM). It dissolves in 4 parts of cold and equal parts of boiling water, the solutions having a neutral reaction. Cold alcohol of 80 per ct. takes up only $\frac{1}{34}$ of this salt, if hot a larger quantity. Otherwise it behaves like chlorate of potash. Adhering *chloride of sodium* is known by

the white turbidness with nitrate of silver; *ammoniacal salts* by the odour they evolve on addition of potash solution; and *carbonate of soda* by its alkaline reaction and effervescence with dilute acids.

NATRIUM OXIDATUM MARGARICUM ET OLEICUM.

Sodæ Margaras et Oleas.—Margarate and Oleate of Soda.—Medicinal Soap.

FORMULA OF THAT PREPARED WITH OLIVE OIL:
$2(NaO + C_{36}H_{33}O_3) + (NaO + C_{34}H_{33}O_3)$.

FORMULA OF THAT PREPARED WITH ALMOND OIL:
$3(NaO + C_{36}H_{33}O_3) + (NaO + C_{34}H_{33}O_3)$.

Preparation.—5 Parts of pure Olive oil are mixed in a porcelain or earthenware vessel with 2 parts of freshly-prepared solution of caustic soda, spec. grav. 1·333, and the whole, being very frequently stirred, is allowed to remain at the ordinary temperature (in winter in a moderately warm room) until it is so stiff as to be almost brittle. A quantity weighing 7 pounds would require from 8 to 10 days. If required in less time, the digestion must be carried on at a gentle heat. The dish is then warmed in a sand bath, and a *little water* added, if during the digestion it has become too dry to form a smooth thin paste on warming. The soft thick fluid mass is poured into a box, from 1 to 1½ inches high and lined with writing-paper; after allowing it to stand a couple of days in a cool place, it is cut into long pieces, thoroughly dried at a very gentle temperature, and kept in a dry place. The yield will be about $\frac{1}{10}$ less than the materials employed.

The method of preparation is entirely the same when almond oil is substituted for olive oil.

Some Pharmacopœias recommend *the soap to be*

salted. For this purpose the soap is dissolved in *three times its weight of water*, and a concentrated solution of salt added (to 4 parts of solution of soap 1 part of salt); it is allowed to remain a few minutes over the fire, being well stirred the whole time, and then placed in a cool spot. When thoroughly cold the soap which separates and solidifies on the surface is thrown on a linen strainer, washed with a small quantity of cold water, and well pressed; the dish is then cleaned, the crumbling mass returned to it, warmed until it forms a smooth mass, and poured into a mould as before.

Recapitulation. Olive oil is a mixture of about 70 parts oleine and 30 parts margarine. Oleine and margarine, from the manner in which they are decomposed by several bases (as potash, soda, lime, oxide of lead, &c.), may be considered as neutral salts of glycerine ($=C_6H_7O_5$) combined with oleic acid ($=C_{36}H_{33}O_3$) and margaric acid ($=K_{34}H_{33}O_3$). Oleine is therefore olcate of glycerine $=C_6H_7O_5+C_{36}H_{33}O_3$; its atomic weight $=1038+3413=4451$; and margarine is margarate of glycerine $=C_6H_7O_5+C_{33}H_{33}O_3$; atomic weight $=1038+3263=4301$. 70 Parts of oleine and 30 parts of margarine correspond, therefore, to about 2 at. of the former and 1 at. of the latter. When the olive oil comes in contact with soda, the latter, being a powerful base, displaces, even at the ordinary temperature, the weaker base, glycerine, and at the same moment combines with 1 at. of water to a hydrate. The new compounds are neutral salts, containing 1 at. of acid to 1 at. of oxide:—

2 at. $C_6H_7O_5+C_{36}H_{33}O_3$, 1 at. $C_6H_7O_5+C_{34}H_{33}O_3$, 3 at. NaO and 3 at. HO, form 2 at. $NaO+C_{36}H_{33}O_3$, 1 at. $NaO+C_{34}H_{33}O_3$, and 3 at. $C_6H_7O_5+HO$.

13203 Parts of olive oil require, therefore, 1170

parts of anhydrous soda, or 4875 parts of caustic soda solution, spec. grav. 1·333 (containing 24 per ct. of soda), or 5 parts of olive oil 1⅚ parts of solution. In the proportions given the soda solution is slightly in excess, as during the process a portion of the soda will, from the action of carbonic acid in the air, be converted into carbonate, and its saponifying action destroyed. If, however, as most Pharmacopœias direct, 2½ parts of pure soda solution, spec. grav. 1·333, are taken to 5 of oil, there always remains a considerable excess of soda in the soap, which, gradually changing to carbonate, effloresces and covers the soap with a white powder. The liberated glycerine remains mixed with the soap; the latter also contains, even when apparently quite dry, a certain quantity (about ¼) of water combined with it; consequently its yield will nearly equal in weight that of the oil and soda employed. The rest of the manipulation requires no explanation.

Almond oil contains oleine and margarine, but only 24 per ct. of the latter. 76 Parts oleine and 24 of margarine correspond to 3 at. of the first, =13353, and 1 at. of the last, =4301. The process is the same as with olive oil, only that 1 at. of almond oil, =13353+4301=17654 parts, require 4 at, =1560 parts of caustic soda, or 6500 of solution, spec. grav. 1·333; that is, to 5 parts of almond oil 1⅚ parts of solution.

The reason for salting the soap lies in the insolubility of the latter in a solution of common salt, and thus the glycerine, with any excess of alkali present, is removed from it; this always causes a slight contamination with common salt, which cannot be removed without loss, as pure water instantly exerts a soluble action on the soap when the saline solution has been strained.

Properties.—From pure olive or almond oil, medicinal soap is a white, solid, homogeneous mass, with a slight peculiar odour, and disagreeable,

rather biting, caustic taste, but not at all corrosive. In the air it undergoes no change; in the heat it fuses, and at a high temperature decomposes, leaving a carbonaceous residue, containing carbonate of soda. It is readily soluble in alcohol and in water, the solutions have an alkaline reaction. Ether abstracts but little from the soap if it has been salted, otherwise it dissolves out all the glycerine, and on evaporation its residue has a distinctly sweet taste. If a watery solution of soap gives off fatty globules on standing, the soap contains *free oil*. If it is not entirely soluble in alcohol, but when well washed with it leaves a white pulverulent residue, soluble in water and effervescing on the addition of acids, *carbonate of soda* is present. In this case the soap becomes covered with a white efflorescence after some time. If not well dried, the soap when kept some time in closed vessels acquires a dark colour and rancid smell. If it has a corrosive taste, *caustic soda* has not been altogether removed.

NATRIUM OXIDATUM PHOSPHORICUM.

Sodæ Phosphas.—Phosphate of Soda.

FORMULA: $2NaO + HO + P_2O_5 + 24Aq.$

Preparation.—(a) From bones.—To a mixture of 5 parts of concentrated sulphuric acid and 25 of water are gradually added, in a leaden vessel, with constant stirring, 6 parts of white bone ash, finely powdered; the vessel is then placed over the fire, and the paste well stirred for one day, the water which evaporates being replaced. The mass is now mixed with as much water as was used to dilute the acid, placed in a bag to strain, and the liquid returned until it runs off clear; when it has drained as much as possible the liquid is pressed,

twice mixed with 40 parts of water, and strained; the liquids are then mixed, and evaporated to about 12 parts. After standing 24 hours the liquid is strained from the silky crystalline mass which it contains, and again diluted with 24 parts of water, warmed and treated with a solution of carbonate of soda as long as this causes a precipitate. From 6 to 7 parts of crystallized soda will be sufficient. When the whole has been warmed for half-an-hour, and a few drops of solution of soda cause no turbidness in a filtered portion, it is allowed to cool and subside, then set aside to crystallize. After obtaining one or two crops the mother liquor is tested with hydrochloric acid for carbonate of soda, and, if this is present, is set aside for neutralizing a fresh quantity of acid. The crystals, if free from carbonate, are spread on filtering paper, dried in the air, and kept in a cool spot. The product is somewhat more than the weight of carbonate used.

(*b*) *With pure phosphoric acid.*—The last traces of sulphuric acid and lime are removed from the salt (*a*) only by numerous re-crystallizations, which entail considerable loss. For analytical purposes it is better to add to pure phosphoric acid solution, in a porcelain dish, pure crystallized carbonate of soda as long as it causes an effervescence, and until the acid reaction is exchanged for an alkaline one. 7 Parts of acid, spec. grav. 1·160, require 6 parts of soda. It is placed in the cool to crystallize, the crystals separated, spread on filtering paper to dry, and kept in a cool place. The mother liquor, on evaporation, yields fresh quantities of crystals. The product will equal in weight the phosphoric acid used.

Recapitulation.—(*a*) The theory of the action of sulphuric acid on bones has been already described under Phosphoric Acid. The carbonate of soda, like ammonia, precipitates from the acid solution

(biphosphate of lime) insoluble basic phosphate of lime, and the carbonic acid is evolved. On this account the quantity of phosphate of soda obtained is less than that calculated from the phosphoric acid contained in bones. The trace of sulphate of lime in the acid liquid is at the same time decomposed by the carbonate of soda, carbonate of lime being precipitated, and sulphate of soda remaining in the solution. Lastly, the magnesia in the bones is precipitated as basic carbonate of magnesia. To cause the carbonic acid to be entirely given off, the solution is warmed; this also facilitates the precipitation of the carbonate of lime. To precipitate the lime entirely a considerable excess of carbonate of soda is requisite, and on this account the last crystals of phosphate of soda contain carbonate as well as sulphate of soda, and consequently must not be mixed with those first formed.

(*b*) The phosphoric acid drives off the carbonic acid, and combines, with excess of soda, to form a basic salt, in which the third atom of base is replaced by water:—

1 at. P_2O_5, 2 at. $NaO + CO_2$, and 25 at. HO, form
1 at. $2NaO + HO + P_2O_5 + 24Aq.$, and
2 at. CO_2.

900 Parts of anhydrous phosphoric acid, or 3912 parts of spec. grav. 1·160 (which contain 23 per ct. of anhydrous acid) require 3580 parts of crystallized carbonate of soda (containing 10 per ct. water). The last crop of crystals in this case may also contain carbonate of soda, and if so they must be kept unmixed with the other.

Properties.—Basic phosphate of soda crystallizes in transparent rhombic prisms and tables, which are odourless and of an agreeable cooling saline taste. In the air it effloresces, slightly at the

ordinary temperature, but much more readily in warm air. Heated more strongly, the crystals fuse in their water of crystallization, and the dried salt has the formula $2NaO + HO + P_2O_5$; if this is heated to redness the basic atom of water is driven off, the salt fusing to a clear mass, which is opaque on cooling. The fused salt is stochiometrically a neutral one, the so-called *pyrophosphate of soda;* the great difference between which and the ordinary basic phosphate of soda is, that it gives, with nitrate of silver, a white precipitate ($2AgO + P_2O_5$), whilst the latter gives a yellow one ($3AgO + P_2O_5$). The precipitate dissolves in 4 parts of cold and in 2 of hot water, but is insoluble in alcohol; the solution has a distinctly alkaline reaction; should it give an effervescence on supersaturation with hydrochloric acid, it contains *carbonate of soda;* a yellow precipitate, caused by passing sulphuretted hydrogen through the acid solution, and readily soluble in carbonate of ammonia, indicates *arsenious acid,* which arises from the employment of either sulphuric acid or phosphorus containing arsenic. If properly prepared, however, the phosphoric acid from the biphosphate of lime cannot contain arsenic, as with the basic phosphate of lime the arsenious acid is precipitated as a lime salt. *Sulphate of soda* is detected in the solution acidified with nitric acid, by nitrate of baryta; *chloride of sodium* by nitrate of silver; traces of either of these salts will, however, be unimportant for medicinal purposes. *Lime* is detected by neutral oxalate of potash, and after separating the lime, ammonia will determine the presence of *magnesia.* If magnesia is suspected, the lime must not be thrown down by oxalate of ammonia, for the magnesia would immediately precipitate as ammonio-phosphate of magnesia. Hydrosulphate of ammonia must cause no change; a black precipitate with it indicates *iron* or *copper;*

the former metal will give a bluish one with tannin.

NATRIUM OXIDATUM SUBSULPHUROSUM.

Sodæ Hyposulphas.—Hyposulphite of Soda.

FORMULA: $NaO + S_2O_2 + 5HO$.

Preparation.—6 Parts of effloresced sulphate of soda, thoroughly dried at a gentle heat, is intimately mixed with 2½ parts of finely powdered wood charcoal; the mixture pressed into a black lead or Hessian crucible, the cover fastened on with wire, and placed in a strong wind furnace; the fire is applied gently at first, but increased after half-an-hour to a bright red heat, and continued at this for an hour uninterruptedly. In order to insure the entire decomposition of the sulphate of soda, the contents of the crucible must not weigh more than one pound. After allowing it thoroughly to cool, the agglutinated contents of the crucible are powdered, dissolved in 24 parts of water, the carbon separated by filtration and $\frac{1}{24}$ of the solution by weight set aside; the remaining $\frac{23}{24}$ are treated with washed sulphurous acid gas—prepared as directed under the article "ACIDUM SULPHUROSUM" from 1 part of freshly heated and coarsely powdered wood charcoal, and 8 parts of concentrated sulphuric acid—until a small portion withdrawn on a glass rod no longer gives a black colour with nitrate of silver, but a pure white one. 1 Part charcoal and 8 sulphuric acid will effect this. During the treatment with sulphurous acid the solution must be cooled with water, snow, or ice. The evolution vessel is instantly removed, the solution filtered and the $\frac{1}{24}$ part added; when after slowly evaporating to a syrupy consistence, it is placed in the cool to crystallize. If after

remaining quiet for some days it fails to crystallize, it must again be gently warmed for a short time ; it then generally happens that the whole mass becomes solid on cooling. The compact crystalline mass or single crystals are now spread on filtering paper, dried in the air or with an extremely gentle heat, and kept in a closed vessel. The mother liquor will yield more crystals on evaporation. The product will weigh about 9 parts.

Hyposulphite of soda is also formed on exposing to the air finely powdered sulphuret of sodium, prepared as just directed ; in this case however the salt will be contaminated with carbonate of soda (*vide* KALIUM SULPHURATUM).

Recapitulation. — At a red heat the charcoal abstracts from the sulphate of soda all its oxygen, forming if in excess, carbonic oxide gas, whilst sulphuret of sodium remains as a dark yellow mass :—

1 at. $NaO + SO_3$, and 4 at. C, form
1 at. NaS, and 4 at. CO.

890 Parts of dried sulphate of soda require 300 parts of pure carbon, but as wood charcoal is always impure more must be used, and an excess is immaterial being separated during filtration. The effloresced sulphate of soda is, on account of its lightness and porosity, preferable to that which has been at once heated to dryness. When the solution of sulphuret of sodium thus obtained is subjected to the action of sulphurous acid, there is formed with the decomposition of water, sulphate of soda and sulphuretted hydrogen :—

2 at. NaS, 2 at. SO_2, and 2 at. HO, form
2 at. $NaO + SO_2$, and 2 at. HS.

By the continued action, sulphurous acid and the sulphuretted hydrogen are mutually converted into sulphur and water :—

1 at. SO_2, and 2 at. HS, form
3 at. S, and 2 at. HO.

and of the 3 at. of sulphur liberated, the sulphite of soda takes up 2 at. whilst 1 at. precipitates :—

2 at. $NaO + SO_2$, and 3 at. S, form
2 at. $NaO + S_2O_2$, and 1 at. S.

The sulphuret of sodium, from 1780 parts (2 at.) of anhydrous sulphate of soda, requires 1200 parts of anhydrous sulphurous acid, which will be formed from 1500 parts of anhydrous, or 1838 parts of the mono-hydrated acid when treated with charcoal. That the process is really as above described and not explicable by the formula :—

2 at. NaS, and 3 at. SO_2, form
2 at. $NaO + S_2O_2$, and 1 at. S.

is evident, by the large quantity of sulphuretted hydrogen evolved, and little sulphur precipitated. Although a rather considerable portion of sulphuretted hydrogen escapes decomposition by sulphurous acid, yet there is more than sufficient sulphur present (as shown by that which precipitates) although less than theory would indicate, to convert the whole of the sulphuret of sodium into hyposulphite of soda.

By testing with nitrate of silver the point is readily ascertained at which the action of the sulphurous acid should be discontinued ; for so long as a trace of sulphuret of sodium remains, it (from the formation of sulphuret of silver) acquires a black colour, and only when all the sulphuret is converted into hyposulphite of soda, the silver salt causes a white precipitate, which on more hyposulphite being added dissolves. After filtering the sulphur from the solution, the $\frac{1}{24}$ of sulphuret of sodium is added to prevent the decomposition of the hyposulphite of soda, by action of the air and heat.

Without this precaution a portion of the hyposulphite of soda would separate into sulphite of soda and free sulphur :—

1 at. $NaO + S_2O_2 = 1$ at. $NaO + So_2$, and
1 at. S ;

whilst the sulphite of soda formed, gradually abstracts oxygen from the air, and forms sulphate ; but when sulphuret of sodium is present, this being more readily oxidizable, is first acted on by the air and converted into hyposulphite of soda. More than $\frac{1}{24}$ should not be added, otherwise an excess will be present and render the product impure. On account of the ready solubility of the hyposulphite of soda, the solution must be tolerably concentrated.

Properties.—The hyposulphite of soda crystallizes in clear rectangular flattened prisms, but generally forms a crystalline mass ; it is odourless, of a mild saline, somewhat hepatic taste. In the air it remains dry, but effloresces slightly in a warm atmosphere. Heated it fuses, giving off watery vapours and sulphuretted hydrogen, then becomes dry, and again liquid at a red heat, whilst sulphur sublimes, and on cooling a dark yellow mass of an hepatic smell and taste remains. The sulphuretted hydrogen is formed by the decomposition of a portion of the water by a part of the hyposulphite of soda, which is at the same time converted into sulphate of soda :—

1 at. $NaO + S_2O_2$, and 1 at. HO, form,
1 at. $NaO + SO_3$, and 1 at. HS.

The greater portion of the hyposulphite of soda separates into sulphate of soda, sulphuret of sodium, and free sulphur :—

4 at. $NaO + S_2O_2$, form
3 at. $NaO + SO_3$, 1 at. NaS, and 4 at. S.

It dissolves in less than its weight of cold water ; the solution has an alkaline reaction, in alcohol it is

insoluble. Nitrate of silver causes a white flocculent precipitate of hyposulphite of silver which is readily soluble in excess of hyposulphite of soda. If the precipitate is not quite white, but grey or black, it contains sulphuret of silver, and the salt is contaminated with *sulphuret of sodium*. The colour of the precipitate is to be noticed at its first formation, as it gradually acquires a yellow-brown, and finally a black colour owing to its separation into sulphuret of silver and free sulphuric acid :—

$$1 \text{ at. } AgO + S_2O_2, \text{ form}$$
$$1 \text{ at. } AgS, \text{ and } 1 \text{ at. } SO_3.$$

If acetic acid causes an effervescence in the solution of hyposulphite, *carbonate of soda* is present; and should chloride of barium cause a white precipitate in it when acidified, *sulphate of soda* also, from which the preparation cannot be easily freed.

NATRIUM OXIDATUM SULPHURICUM.

Sodæ Sulphas.—Sulphate of Soda.—Glauber's Salts.

Formula : $NaO + SO_3 + 10HO$.

Preparation.—Sulphate of soda is a secondary product, only requiring purification, in so many processes, as the manufacture of hydrochloric and nitric acids, the precipitation of metallic sulphates by carbonate of soda and so on, that its direct fabrication is seldom necessary. The residues from the distillation of hydrochloric and nitric acids is a bisulphate, to neutralize this with carbonate of soda would be too expensive; the cheapest and simplest method is by calcination, but where this operation is inconvenient, the following may be employed :—

The acid sulphate of soda is dissolved in an earthen dish, or, by considerable quantities, in a

wooden tub, in ten parts of water, and lime made to a thin paste with water is gradually added as long as the mixture continues to redden litmus paper. The milk of lime must be very gradually added, as it does not at once combine with the acid, and any excess of lime is accompanied by a corresponding loss of sulphate of soda. When saturated, it is allowed to subside, decanted, the residue thrown on a strainer, and washed with hot water so long as the liquid passing off has a saline taste. The mixed liquid is then boiled in a lead or clean copper vessel until a small portion withdrawn from it gives signs of crystallization on cooling; then filtered whilst hot, and the filtrate kept in a cool place for some days. The crystals are freed from the mother liquor, and the latter evaporated. The first and second crop are generally pure, but after that they are often yellow ,and require to be crystallized. The crystals are spread out on a sieve covered with bibulous paper, dried in the air, and kept in a cool place.

The brown mother liquor is evaporated to dryness, and employed as anhydrous sulphate of soda, where a little colouring matter and sulphate of lime are not of consequence.

Recapitulation.—When acid sulphate of soda is saturated with lime, the slightly-soluble sulphate of lime is formed, and a hydrated salt $= CaO + SO_3 + 2HO$ precipitates, whilst neutral sulphate of soda, with a slight trace of sulphate of lime, remains in solution; on evaporation, the latter separates, and may be removed by filtration. There is no fear that with the crystals of the Glauber's salts gypsum will be thrown down, as this is not more soluble in hot than in cold water.

Properties.—Neutral sulphate of soda crystallizes in large, clear, oblique, rhombic fluted prisms, which are odourless, and possess a faintly saline, cooling, bitter taste. In the air, from loss of water,

they are quickly covered with a white light powder (anhydrous sulphate of soda,) into which they after some time fall. Heated, they fuse in their water of crystallization, and, on losing this, form a dry mass, which heated to redness becomes fluid, without decomposing. Of water at the ordinary temperature it requires 3 parts for its solution, but at 90° Fah. less than half its weight; the solution has a neutral reaction. Alcohol has no effect on it. If ammonia causes with it a white precipitate, soluble in sal ammoniac, *magnesia* is present; if insoluble, it is *alumina*. If oxalate of ammonia causes a precipitate, *lime* is present; and an evolution of ammonia, on the addition of caustic potash, denotes *ammoniacal salt*. *Chlorides* are detected by nitrate of silver, *iron* by tannin, *copper* by ferrocyanide of potassium, or a clean piece of iron on which the copper precipitates.

PICROTOXINUM.

Picrotoxine.

FORMULA: $C_{12}H_7O_5$.

Preparation.—Cocculus Indicus is bruised, the hulls separated by sifting, the inner portion powdered, warmed in a copper or iron vessel, and strongly pressed. The residue is again bruised up, the powder digested in a flask, or in large quantities in a still, with three times its weight of alcohol of 80 per ct., for one day, then pressed, and the residue treated twice again with the same quantity of alcohol, to the alcoholic tincture $\frac{1}{6}$ its volume of water is added, the alcohol distilled off, the residue poured into a copper vessel, and, after adding a moderate quantity of powdered wood charcoal, evaporated to dryness with a gentle heat. The dried mass is finely powdered, digested with ether three

times, in a closed bottle at the ordinary temperature; $\frac{1}{8}$ its weight of water is then added to the ethereal tincture, the ether distilled off, the residue gently warmed in a porcelain dish until the smell of ether has entirely disappeared, and then allowed to cool. The fatty substance, which swims on the surface, is separated by filtration, the fat washed with alcohol of 60 per ct., and the filtrate evaporated to crystallization. After the picrotoxine has crystallized, it is pressed between filtering paper, again dissolved in three times its weight of boiling alcohol of 80 per ct., and allowed to crystallize. The produce from 8 pounds of berries will be from 1 to $1\frac{1}{2}$ ounces.

Recapitulation.—Picrotoxine exists in the fleshy part of the Cocculus Indicus berries in an uncombined state; according to Pelletier, the shells contain an alkaloid, Menispermin, they must therefore be separated. By pressing, a great portion of the fatty matter they contain is removed, which would be troublesome in the next operation of exhausting, &c. Alcohol takes up the picrotoxine easily and completely, and with it the colouring matter also; to remove this, the alcoholic extract, mixed with fine charcoal that it may be readily powdered, is digested with ether, which only dissolves the picrotoxine and a little fat. As soon as the ether has evaporated the fat rises to the surface, and when it has solidified may be removed by filtration. To remove the last trace of fat, the crystals are pressed between blotting paper, and recrystallized.

Properties.—Picrotoxine forms white crystalline crusts, or brilliant needles of an insupportably bitter taste, but odourless. It is unchanged in the air, heated it fuses, and gives off volatile products, having an acid reaction, a carbonaceous residue being left, which must be entirely combustible in the air. It dissolves in 150 parts of cold water, and in 25 of boiling; in 10 parts of cold and in its own

weight of boiling alcohol of 80 per ct.; 2½ parts of ether dissolve it; the solutions have no action on vegetable colour. It is readily taken up by caustic alkalies.

PIPERINUM.

Piperine.

FORMULA: $C_{70}H_{37}N_2O_{10} + 2HO$.

Preparation. — A convenient quantity of black pepper is coarsely powdered, treated with twelve times its weight of cold water and, frequently shaken, is allowed to digest a few days; after subsiding, the clear liquid is poured off, the residue again digested and pressed. The residue is now digested three times with alcohol of 80 per ct., the alcohol each time being three times the weight of the pepper. The filtered tinctures are mixed with ⅛ their volume of water, and distilled, the residual liquid is then evaporated in a porcelain dish to the consistence of an extract. After standing some days in a cool place, this is exhausted with water, the insoluble portion again dissolved in alcohol, and hydrate of lime, equalling in weight $\frac{1}{16}$ of the pepper, is digested with it for one day in a warm place, then filtered, and evaporated to crystallization. The last portion of the mother liquor, which contains a good deal of resin, may be thrown away; the crystals (excepting perhaps a few which form at first) are finely powdered, treated in the cold with a small quantity of ether, dissolved in alcohol, digested with animal charcoal that has been purified with hydrochloric acid, filtered, and the alcohol distilled; the residue is set aside to crystallize. The product from 8 pounds of pepper will be rather more than 3 ounces.

Recapitulation.—Black pepper contains piperine in an uncombined state, cold water, whilst scarcely acting on the piperine, dissolves the extractive matter; alcohol dissolves the piperine and the resin. As after treating with water, a portion of the extractive matter is always left behind, and becomes dissolved by the alcohol, the spirituous extract is again washed with water to remove it. The residue again dissolved in alcohol still contains a large quantity of resin, which forms with lime a compound but slightly soluble. By agitating with ether the last portions of resin are withdrawn, with but little loss of piperine, whilst the charcoal removes the colouring matter. The last operation generally requires to be repeated.

Properties.—Piperine crystallizes in moderate sized white or pale yellow crystals, which are odourless, and if white, almost tasteless; the coloured, from the adherent pungent matter, have the taste of pepper. Heated it fuses, at a higher temperature it gives off volatile ammoniacal products, leaving a carbonaceous residue which must be entirely combustible. Piperine is not soluble in cold, and but slightly so in hot water; it is soluble in 30 parts of cold or in its own weight of boiling alcohol; ether on the other hand dissolves only $\frac{1}{100}$ part; the solutions do not affect litmus or turmeric paper. In acetic acid it is readily soluble.

PLATINUM NIGRUM.

Platinum Black.

FORMULA: Pt.

Preparation.—5 Parts of hydrated chloride of platinum are dissolved in a porcelain dish with 100 parts of water, to the solution are gradually added 7

parts of *crystallized carbonate* of *soda* and afterwards 1 ⅔ parts of *dry formiate* of soda. The whole is allowed to digest 1 or 2 days at the ordinary temperature with frequent agitation. It is now warmed in a sand-bath until the supernatant liquid has become colourless, then filtered, the precipitate washed with water and dried with a gentle heat. Its weight equals 2 parts.

Dobereiner's method, adding a large excess of soda to a platinum solution (3 parts of soda to 1 of the platinum salt) and then reducing with alcohol or sugar, I have not found to answer perfectly.

Recapitulation.—When solutions of chloride of platinum and formiate of soda come in contact, the sodium combines with the chlorine, whilst the oxygen of the soda instead of oxidizing the platinum, forms with the elements of the formic acid, carbonic acid, carbonic oxide and water, whilst the platinum, in the metallic state, precipitates as a fine black velvety powder. Owing to the evolution of carbonic acid, the reaction is accompanied by effervescence :—

1 at. $Pt + Cl_2$ and 2 at. $NaO + C_2HO_3$, form
2 at. NaCl, 1 at. Pt, 2 at. CO, 2 at. CO_2, 2 at. HO.

3018 Parts of chloride of platinum require 1705 parts of formiate of soda. One half of the formiate of soda may be saved by first combining the chlorine of the platinum salt with soda, (using sufficient of the latter to act as a base to the oxide of platinum,) forming a platinum and soda salt, which being readily soluble remains mixed with the chloride of sodium ; for this purpose only ¼ more soda is requisite :—

2 at. $PtCl_2$ and 4 at. $NaO + CO_2$, form
4 at. NaCl, 4 at. CO_2, and 2 at. PtO_2 ;
further
2 at. PtO_2 and 1 at. $NaO + CO_2$, form
1 at. $NaO + 2\ PtO_2$ and 1 at. CO_2.

6036 Parts of crystallized chloride of platinum require 8950 parts of crystallized carbonate of soda. Formiate of soda decomposes the soda and platinum salt thus,—the oxygen of the oxide of platinum passes to the formic acid with which, besides water, it forms carbonic acid that is partly evolved and partly combines with the soda separated from the platinum salt; the reduced platinum precipitating:—

1 at. $NaO + 2\ Pt.O_2$ and 2 at. $NaO + C_2HO_3$, form 3 at. $NaO + CO_2$, 2 at. HO, 1 at. CO_2, and 2 at. Pt.

6036 Parts of crystallized chloride of platinum require therefore in this case only 1705 parts of formiate of soda; the proportions 5 parts and 1 $\frac{2}{3}$ parts contain the latter slightly in excess, so that it causes the precipitation of the platinum with certainty. The process of reduction goes on but slowly in the cold, it is greatly facilitated by warming; it is however not advisable at once to warm the mixture, otherwise the separation of the platinum takes place so rapidly that it forms a compact mass on the side of the vessel and the aim of the process is defeated. For the same reason the liquid must be very dilute. The liquid filtered from the platinum black is thrown away as worthless.

In Dobereiner's process sugar or alcohol is made to replace the formiate of soda. In this case other products of decomposition as acetic acid, aldehyde, formic acid, &c.; these, however, are not sufficiently studied for a correct stochiometrical plan to be drawn of them.

Properties.—Pure platinum black is a soft, heavy, black, odourless, and tasteless powder. By heating to redness it acquires, with an aggregation of its particles a gray colour, becoming the so-called spongy platinum, without undergoing any further change. It is perfectly insoluble either in hydrochloric acid, nitric acid, or water; in aqua regia it readily dissolves. Its most peculiar property is

that of oxidizing alcohol, forming acetic acid. Placed under a bell-glass with a small dish filled with alcohol, the latter after about a quarter of an hour acquires a powerful acid reaction and has a strong smell of acetic acid. Platinum black condenses in its extremely fine pores a considerable quantity of oxygen and as this is transferred to the alcohol, the platinum black again condenses a fresh portion, keeping up a constant supply. The alcohol forms acetic acid and water:—

1 at. $C_4H_6O_2$ and 4 at. O, form
1 at. $C_4H_3O_3$ and 3 at. HO.

PLUMBUM CHLORATUM.

Plumbi Chloridum.—Chloride of Lead.

Formula: PbCl.

Preparation.—4 Parts of sugar of lead are dissolved in 12 parts of pure water, and pure hydrochloric acid (about 3 parts spec. grav. 1·130) is added as long as a precipitate is caused. The precipitate thrown on a filter is washed a few times with pure water and dried at a moderate temperature. The yield will be about $2\frac{3}{4}$ parts.

Recapitulation.—Acetate of lead = PbO + $\bar{A}$ + 3HO on the addition of hydrochloric acid gives off its acetic acid and water, forming water and chloride of lead which is very slightly soluble, and mostly precipitates as a white crystalline powder:—

1 at. PbO + $\bar{A}$ + 3HO and 1 at. HCl, form
1 at. PbCl, 1 at. $\bar{A}$, and 4 at. HO.

2370 Parts of acetate of lead require 1750 of hydrated hydrochloric acid spec. grav. 1·130 (= 26 per ct. anhydrous). By washing, the liberated acetic acid

and any excess of hydrochloric acid are removed, but as this causes a slight loss of chloride of lead, it is not long continued, the last portions of acetic and hydrochloric acids being entirely given off on drying.

After adding sufficient carbonate of lime to neutralize the hydrochloric acid, the acetic acid in the filtered liquor may be re-obtained by distillation.

Properties.—The chloride of lead is a white crystalline powder (consisting of fine needles) odourless and of a sweetish astringent taste. In the air it undergoes no change. Heated it fuses, forming when cold a horny semi-transparent mass, which at a higher temperature is completely volatile without decomposition. Water at the ordinary temperature dissolves $\frac{1}{30}$, boiling $\frac{1}{20}$ of this salt; the solution has an acid reaction. Alcohol does not dissolve it. If it contains *copper* it acquires a greenish tint on becoming moist in the air; and ammonia causes the deep blue solution.

PLUMBUM IODATUM.

Plumbi Iodidum.—Iodide of Lead.

FORMULA: PbI.

Preparation.—1 Part of nitrate of lead is dissolved in 20 parts of pure water and mixed with a solution of 1 part of iodide of potassium in 8 parts of water; the precipitate is allowed to subside, thrown on a filter, well washed with cold water and dried with a gentle heat. The product will be $1\frac{2}{3}$ parts.

Acetate of lead cannot be substituted for the nitrate as the acetate of potash that results is a solvent of iodide of lead.

Recapitulation.—Nitrate of lead and iodide of potassium in their aqueous solution are mutually

decomposed into nitrate of potash and iodide of lead :—

1 at. $PbO + NO_5$ and 1 at. KI, form
1 at. PbI and 1 at. $KO + NO_5$.

2069 Parts of nitrate of lead require 2076 parts of iodide of potassium. In this case the whole of the lead and iodine is not precipitated, the iodide being slightly soluble in water; the loss is however far less than with acetate of lead.

Properties.—Iodide of lead thus formed is an odourless and tasteless yellow powder. When heated it becomes reddish yellow, then darker, and finally fuses to a dark brown liquid which gives off iodine and on cooling forms a lemon-yellow basic compound. It dissolves in 1990 parts of cold and in 1330 parts of boiling water; the solutions are colourless, the hot one depositing as it cools large brilliant golden scales. 4500 Parts of cold alcohol of 80 per ct. and rather less of hot alcohol, dissolve 1 part of iodide of lead, forming pale straw-coloured solutions; the hot one deposits on cooling excessively fine glistening scales. Ether acts on it like alcohol, also giving a pale straw-coloured solution.

PLUMBUM OXIDATUM.

Plumbi Protoxidum.—Massicot.—Litharge.

FORMULA: PbO.

Preparation.—(*a*) From *carbonate of lead.* This is obtained as a secondary product in many processes (KALI. ACET.; NATR. ACET.); a porcelain or Hessian crucible is ⅔ filled with it, covered and exposed to a gentle red heat until all the powder has become yellow, and a small portion dissolved in nitric acid gives no effervescence. The crucible is then removed, and, when cold, the contents transferred to

a stoppered bottle. The product from 4 parts of carbonate exceeds 3 parts.

(b) From *nitrate of lead.*—Nitrate of lead occurs as a secondary product in some preparations (as that of brown peroxide of lead), or 3 parts of pure nitric acid 1·20, and 3 parts of pure water are poured on 1 part of finely-shredded metallic lead: when there is no further action and metallic lead still remains unacted on, the flask is placed in a sand bath until the metal is dissolved, filtered if necessary whilst warm, and set aside. After some days, the crystals which form are separated from the mother liquor, and the latter evaporated to obtain a fresh portion. The salt is spread on filtering paper and dried with a gentle heat. It will weigh about 1½ parts.

A porcelain or Hessian crucible is now heated to low redness, and the powdered salt thrown in by spoonfuls, taking care that one portion is decomposed before another is added; when red fumes are no longer given off a moderate heat is continued for ½ of an hour, the crucible removed, and the contents placed in a closed bottle. 1 Part of lead gives 1½ of oxide.

Recapitulation.—*(a)* Carbonate of lead is a neutral salt = $PbO + CO_2$. At a red heat it gives off its acid, acquiring a yellow colour. The heat must not be too high, otherwise the oxide fuses.

(b) Metallic lead is readily dissolved by dilute nitric acid; 3 at. of oxygen from 1 at. of acid combine with 3 at. of lead, forming 3 at. of oxide, which unite with 3 at. of nitric acid; whilst the NO_2, nitric oxide, evolved, coming in contact with the air, gives rise to the characteristic brown vapours of hyponitric acid:—

3 at. Pb and 4 at. NO_5, form
3 at. $PbO + NO_5$, and 1 at. NO_4.

3882 Parts of lead require 2700 parts of anhy-

drous or 10,000 parts of nitric acid, spec. grav. 1·20. By the addition of water the partial deposition of the nitrate is prevented. After obtaining several crops of crystals a bluish green salt is generally formed which, as containing copper, is not mixed with that previously crystallized. By heating, the acid is given off, and as this cannot exist in an anhydrous state, it separates into oxygen and hyponitric acid, which are evolved. On account of the force with which the decomposition takes place, the salt must be added gradually and not at once. For the reason given under (*a*) the heat must not be too great.

Properties.—Pure oxide of lead is a clear yellow (canary yellow), odourless and tasteless powder. Exposed for some time to the air it slightly attracts carbonic acid. On heating it acquires a reddish colour, becoming yellow again on cooling. At a strong red heat it fuses to a yellow transparent liquid, and forming, when cold, a yellowish red, heavy, opaque mass, consisting of crystalline scales. By simply fusing oxide of lead, it is never obtained in a transparent state on cooling, although most chemical works assign to it the property; this only occurs when it contains silica, for acquiring which Hessian crucibles afford facilities. The opaque, scaly, crystalline mass is litharge. This is not half fused, as generally stated, but thoroughly fused oxide of lead, as a glance at its formation, by volatilizing lead from its alloys with silver or gold readily proves. Water quite free from air dissolves small portions of lead, which again precipitate as carbonate when the solution is exposed to the atmosphere. Nitric and acetic acids dissolve it entirely to a colourless solution, if with effervescence *carbonic acid* is present; and a blue tint to the solution denotes *copper*. Traces of copper are detected on adding ferrocyanide of potassium to the solution from which nitrate of lead has been decom-

posed by sulphate of soda, if a chocolate-coloured precipitate forms, it is present; any iron present should, previous to the addition of ferrocyanide, be removed by ammonia. *Iron* is detected by the red colour which sulphocyanide of potassium forms with the nitrate (*vide* BISMUTH. NITR.). If nitric acid leaves a portion of oxide undissolved, and of a dark brown colour, it is *peroxide*, and in this case the colour of the oxide is a reddish yellow instead of a clear yellow. A reddish yellow appearance may also be the result of heating too strongly, *i. e.* of incipient fusion, without any peroxide being present. A white residue, on treating with nitric acid, may be due to *oxide of antimony* (in commercial litharge); this residue gives a metallic bead when heated on charcoal and white fumes, with which the latter becomes covered. *Silica* also remains undissolved, but is unchanged when heated on charcoal.

PLUMBUM OXIDATUM ACETICUM BASICUM.

Liquor Plumbi Diacetatis.—Solution of Basic Acetate of Lead.

FORMULA: $PbO + \bar{A}, + xPbO + xAq$.

Preparation.—The processes for this preparation vary in different Pharmacopœias, yielding products not only varying in the relative proportions of acid and oxide, but also in specific gravity; hence the necessity for pharmaceutists adhering to that contained in their own national Pharmacopœia.

As all the different forms cannot here be noticed, three separate ones, the Bavarian, Prussian, and

Baden processes are given, to one of which most of the others approximate.*

(*a*) *According to the Baden Pharmacopœia.* 6 Parts of sugar of lead, 7 parts of finely-powdered litharge, and 30 parts of pure water, are digested for one or two days in a closed flask at a gentle heat, being frequently agitated; filtered when cool, the air being excluded as much as possible, and the filtrate kept in a closed bottle. Its spec. grav. is 1·200.

(*b*) *According to the Prussian Pharmacopœia.* 6 Parts of sugar of lead, 2 parts of litharge, and 20 parts of water are treated in the same manner. Spec. grav. 1·240.

(*c*) *According to the Bavarian Pharmacopœia.* 6 Parts of sugar of lead, 2 parts of litharge, and 11 parts of water; treated in a similar manner. Spec. grav. 1·360.

The Bavarian Pharmacopœia really directs 18 parts of water to be used and then evaporated to the above spec. grav.; but by using only 11 parts for digesting the same end is attained, and more conveniently.

If the solution is of a bluish colour it must be agitated with shavings of metallic lead.

The method, at one time in general use, of forming acetate of lead by boiling litharge with acetic acid in copper vessels, is now, very properly, seldom employed.

Recapitulation.—(*a*) Sugar of lead, the neutral acetate, is capable of combining with and dissolving 2 at. of oxide of lead; so that when it contains the

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* In the London Pharmacopœia the proportions given are 6·75 parts of acetate of lead, 4 of litharge and 20 of water, in which there is a trifling excess of oxide of lead over equal atoms. The spec. grav. is given as 1·260, and the formula should correspond to $C_4H_3O_3 2PbO + xHO$ = bibasic acetate of lead.

largest possible quantity of oxide a tribasic salt is the result :— *

1 at. $PbO + \bar{A} + 3HO$, and 2 at. PbO, form
1 at. $3\,PbO + \bar{A}$, and 3 at. HO.

2370 Parts of crystallized sugar of lead require therefore 2788 parts of oxide of lead, litharge, or 6 of the former to 7 of the latter. In practice we find that with these proportions no perfectly tribasic salt will be formed, as the sugar of lead always leaves a portion of the oxide of lead unacted on, (increasing with the larger proportion of basic salt it contains), either as pure oxide or carbonate of lead, from the action of the carbonic acid of the atmosphere on the basic acetate already formed. The method prescribed in the Baden Pharmacopœia (and indeed those in the other Pharmacopœias) does not form a perfectly tribasic salt; it is only in the proportion of 8 parts of oxide of lead to 6 of sugar of lead that this is effected. This method has also the disadvantage of giving a considerable residue of thick matter, which mostly consists of tribasic acetate, as well as some oxide and carbonate, and if this is left on the filter a loss occurs, whilst by washing to obviate the loss, the spec. grav. of the whole preparation is reduced. To obtain a perfectly soluble and uniform tribasic acetate of lead, the proportions of water, as well as oxide of lead, must be increased. The solution of the oxide of lead, by acetate, occurs with equal certainty at the ordinary temperature, but is facilitated by heat. The air is of course to be carefully excluded, as the carbonic acid it contains converts the basic compound into insoluble carbonate, and soluble neutral acetate :—

* I have never been able to form a salt containing 6 at. of base $6PbO + \bar{A}$.

3 at. $3PbO + \bar{A}$, 4 at. CO_2, and 2 at. HO, form 3 at. $PbO + \bar{A}$, and 2 at. $2(PbO + CO_2) + (PbO + HO.)$

For this reason, the formation of the basic acetate by boiling in the air cannot be recommended. If, as is often the case, the litharge contains oxide of copper, this is dissolved, and the preparation has a blue colour. Metallic lead reduces the oxide of copper, precipitating it in the metallic state, an equivalent of lead, combined with the oxygen from the copper, remaining dissolved.

(*b.*) The proportions in the Prussian Pharmacopœia between sugar of lead, and oxide of lead, are 2 at. and rather more than 1 at., or 4740 and 1580. By taking into consideration the trifling residue, this acetate is a sesquibasic salt $= 3PbO + 2\bar{A}$.

(*c.*) In the Bavarian Pharmacopœia, the proportions being the same, the salt is also sesquibasic, the difference being that the solution is more concentrated, 19 parts containing as much lead salt as 28 parts of the other acetates.

Properties.—Basic acetate of lead is a transparent liquid, having a strong alkaline reaction, odourless, and of a sweet astringent taste. Its spec. grav. and composition vary according to the different forms, but it is well to remark that none of the methods yield a perfectly tribasic acetate of lead. With recently boiled (free from carbonic acid) distilled water, the acetate of lead is miscible, without becoming turbid; with water that has been exposed to the air it becomes opalescent, carbonate of lead depositing, and neutral acetate remaining in solution. Spring water, which contains sulphates and carbonates, as well as free carbonic acid, gives a denser white precipitate of sulphate and carbonate of lead, the chlorides also present form chloride of lead, but this is not in sufficient quantity to precipitate. When exposed to the air, basic acetate of

lead becomes covered, from the action of the carbonic acid, with a white pellicle of carbonate, which after a time precipitates, and is renewed; hence the necessity of keeping the preparation in well-closed vessels. A bluish colour indicates *copper*, arising from the litharge; a yellow colour is generally due to *extractive matter*, from using common vinegar, or *iron* (also from the litharge). The copper is most readily determined by treating with excess of ammonia, and if the solution is blue, supersaturating with acetic acid, and testing with ferrocyanide of potassium, when a chocolate precipitate will be formed. Sulphocyanide of potassium, added to acetate of lead, supersaturated with acetic acid, will give a red colour if iron is present. (*Vide* Bism. Nitr.)

PLUMBUM OXIDATUM MARGARINICUM ET OLEINICUM.

Plumbi Margaras et Oleas.—Emplastrum Plumbi.—Margarate and Oleate of Lead.—Lead Plaster.

Formula:

$$2(2PbO + C_{36}H_{33}O_3) + (2PbO + C_{34}H_{33}O_3).$$

Preparation (a.) — With Litharge. 6⅛ Parts of very finely powdered litharge are mixed with 1¾ parts of water in a copper or earthen vessel, and gently warmed. At the same time 10 parts of olive oil are weighed into a copper vessel, capable of containing 50 parts, and heated, at first gently, until it begins to fume and crackle, when, with constant stirring, the warm mixture of litharge and water is added in very small portions, taking care that one portion is nearly dissolved, or that no more bubbles or aqueous vapours are evolved, before another is added. After the addition of the last portion, heat

for a few minutes, withdraw a small portion and knead it under water; if it is readily worked, without imparting a milkiness to the water, the whole is allowed to cool, and moulded to the required form. If the test is unsatisfactory, the boiling is continued, with the occasional addition of an ounce of warm water, but a quarter of an hour should be ample time.

(*b.*) *With Basic Carbonate of Lead.* 7 Parts of white lead, 3 parts of water, and 10 parts of olive oil, are combined as directed under (*a.*)

Most Pharmacopœias prescribe a larger quantity of carbonate of lead; this excess cannot enter into combination, but remains in admixture.

Recapitulation (*a.*)—Olive oil, as shown under the article NATRIUM OXIDATUM MARGARINICUM, &c., is a mixture of about 70 parts oleine, and 30 parts margarine, its equivalent being 4301 parts. When hot olive oil is mixed with water and oxide of lead, the latter, being a stronger base, combines with the margaric and oleic acids in the oil, the base in the oil, Glycerine, is liberated, and combines with 1 at. of water to form a hydrate. The lead compounds thus formed are insoluble basic salts; 2 at. of oxide being combined with 1 at. of acid:—

2 at. $C_6H_7O_5 + C_{36}H_{33}O_3$ (Oleine), 1 at. $C_6H_7O_5 + C_{34}H_{33}O_3$ (Margarine) 6 at. PbO, and 3 at. HO, form

2 at. $2PbO + C_{36}H_{33}O_3$, 1 at. $2PbO + C_{34}H_{33}O_3$, and 3 at. $C_6H_7O_5 + HO$.

13203 Parts of olive oil require 8364 parts of oxide of lead, and 338 parts of water, or 10 parts of olive oil, $6\frac{1}{3}$ oxide of lead, and $\frac{1}{4}$ part of water; the latter must, however, be considerably increased, as the new compound forms but slowly, allowing the greater part of the water to evaporate, which has the good effect of preventing the mixture from becoming too hot, and boiling over, or igniting.

Without the addition of water, the oleic acid is not separated from the glycerine, and no plaster forms; if a portion of plaster is formed when no water has been added, it is because oil always contains a small quantity, and the remainder must have been derived from the elements of the oil. There being great disadvantages in omitting the water, this process has no practical value. In the method here given, the formation of the plaster is rapid when the oxide of lead is in very fine powder; the mixture of the latter with water must be added warm, otherwise, at the moment of contact with the hot oil, a spirting and boiling up of the mass ensues, from the sudden formation of aqueous vapour. Stirring facilitates the combination, by intimately mixing the particles, and prevents any from adhering to the bottom of the vessel. To a practised workman the tenacity and consistence of the mass indicates when it is entirely formed, and this is more satisfactorily ascertained by kneading a portion of it under water; if the water becomes turbid, free oxide is present, and oil globules will rise to the surface, and this necessitates a continuance of the boiling, with the addition of a little warm water. Lead plaster is often prepared by mixing the lead and oil, then heating, and occasionally adding water; the method previously described will be found the most certain, and quickest.

In moulding up the plaster with water the glycerine will be washed away.

(*b.*) In reviewing the process in which white lead, basic carbonate $= 2(PbO + CO_2) + (PbO + HO)$, is made to replace litharge, it is only necessary to add to the above explanation that carbonic acid is evolved:

2 at. $C_6H_7O_5 + C_{36}H_{33}O_3$, 1 at. $C_6H_7O_5 + C_{34}H_{33}O_3$, 2 at. $(2PbO + CO_2) + (PbO + HO)$, and 1 at. HO, form

2 at. $2PbO + C_{36}H_{33}O_3$, 1 at. $2PbO + C_{34}H_{33}O_3$, 3 at. $C_6H_7O_5 + HO$, and 4 at. CO_2.

13203 Parts of olive oil require 9690 parts of carbonate of lead, or 10 parts to 7. In this case the action is slower, from the oxide being in combination with carbonic acid, which is not readily driven off by the fatty acid; the action is first induced by the atom of free oxide in the white lead. Neutral carbonate of lead ($PbO + CO_2$), as Pfaff has already observed, and I can confirm, gives a useless plaster, which contains but a small portion of the fatty salts of lead. It is evident, however, that the neutral carbonate of lead, which is often obtained as a residuary product, may be made applicable to the manufacture of plaster by the addition of $\frac{1}{3}$ litharge. With basic carbonate of lead a certain quantity of litharge is generally prescribed, but further than to hasten the process, this addition is unnecessary.

Properties.—Lead plaster from oxide is a yellowish white mass, brittle when cold, plastic when warm, insoluble in water or alcohol, and partially soluble in ether, the margarate of lead forming the residue. The plaster from carbonate is white, with, when freshly prepared, a trace of silver gray, this it loses on exposure to the air. Both are chemically identical, the difference in colour arising from the white lead being a purer substance than litharge, which generally contains oxide of iron and copper. I have seen plaster prepared from litharge so white as not to be distinguishable from that prepared with white lead; this is when quite pure oxide has been employed. A darker colour will be due to dirt, or burning during its manufacture. *Free oxide* or *carbonate of lead* is not always to be detected by kneading with water, as both plasters, from their tenacity, may retain it so firmly that the water is not rendered turbid. In litharge plaster the excess may be detected by the naked eye, but in white lead plaster only on digesting with ether, which dissolves the oleate, leaving the margarate of lead and excess of carbonate; if this,

instead of a tenacious mass, forms one that can be readily powdered and becoming discoloured, white lead is present; if the white lead is pure, this crumbling mass, when heated on charcoal, is entirely reduced to a globule of metal, the margaric acid burning. If, besides the metal, a white powder remains, this may be *heavy spar*, *chalk*, or *gypsum*, with which the white lead was contaminated. To determine the nature of this impurity more fully, the plaster is heated in a porcelain crucible, to burn off the organic matter; the oxide of lead is thus reduced to a metal, the chalk remains unchanged, the heavy spar and gypsum are reduced to sulphurets, but, when the carbon is all consumed, are again converted into sulphates by the oxygen of the air. On agitating the residue with water the *gypsum* dissolves, and oxalate of ammonia and chloride of barium cause a turbidness in the solution; effervescence with hydrochloric acid in another portion indicates *chalk;* whilst an insoluble portion, giving no reaction in either case, is probably *heavy spar*.

PLUMBUM SUPEROXIDUM BRUNEUM.

Peroxide of Lead.

FORMULA: PbO_2.

Preparation.—2 Parts of Minium are mixed in a capacious porcelain dish with 4 parts of pure water, 4 parts of pure nitric acid, spec. grav. 1·20, added with constant stirring, and the whole allowed to digest in a sand bath for one day; sufficient water is then added to bring the weight up to 12 parts; it is then poured into a cylindrical vessel to subside. The supernatant clear liquor is decanted, the dark-brown residue thrown on a filter, thoroughly washed with water (until the liquor passing off

neither has an acid reaction nor undergoes a change when treated with sulphuretted hydrogen), then dried, and kept in a vessel from which daylight is excluded. The produce is about $\frac{2}{3}$ the weight of minium used.

Recapitulation.—Minium consists of 3 at. of lead and 4 at. of oxygen; it may also be considered as a compound of 2 at. oxide of lead and 1 at. peroxide of lead, $=2PbO + PbO_2$. Nitric acid dissolves the oxide of lead, leaving the peroxide unacted on:—

1 at. $2PbO + PbO_2$, and 2 at. NO_5, form
2 at. $PbO + NO_5$, and 1 at. PbO_2.

4282 Parts of minium do not really require more than 1350 parts of anhydrous nitric acid, or 5000 parts spec. grav. 1·20; a slight excess is, however, necessary for the complete decomposition of the salt; and besides this, minium of commerce always contains a certain portion of carbonate of lead, as is seen by the effervescense on the addition of the acid. To this carbonate of lead may be ascribed the smaller product of peroxide than calculation would lead us to expect. Nitric acid exerts a very energetic action on minium; digestion for some hours, however, is necessary to free it from the last traces of oxide. Any foreign metallic oxides, as oxide of copper, peroxide of iron, are at the same time dissolved. By dilution with water the crystallization of the nitrate of lead formed is prevented.

The nitrate of lead is obtained by crystallization from the wash water; the last portions of mother liquor, which generally contain copper or iron, are thrown away. On an average, the salt equals in weight the minium employed.

Properties.—Peroxide of lead is a heavy puce-brown powder, odourless and tasteless. It undergoes no change in the air, but in direct sunlight it gives off oxygen, becoming partially converted into

oxide. At a gentle red heat it evolves half its oxygen, pure oxide remaining. In water, alcohol, acetic or nitric acids, it is perfectly insoluble, whilst hydrochloric acid decomposes it, forming water and chloride of lead, and evolving chlorine :—

1 at. PbO_2, and 2 at. HCl, form
1 at. PbCl, 2 at. HO, and 1 at. Cl.

QUININUM PURUM.

Pure Quinine.

FORMULA : $C_{20}H_{12}NO_2 + 3HO = \overset{+}{Q} + 3HO$.

Preparation.—Sulphate of quinine is dissolved, with the assistance of a few drops of dilute sulphuric acid, in twenty times its weight of distilled water, and caustic soda solution added by drops until the liquid acquires a clearly alkaline reaction, and a filtered portion is not rendered turbid by the soda solution. The pulverulent precipitate is allowed to deposit, collected on a filter, well washed with distilled water, and dried by a gentle heat. 10 Parts of sulphate yield 7 parts of quinine.

Recapitulation.—The ordinary (officinal) sulphate of quinine is a basic salt, consisting of 2 at. quinine, 1 at. sulphuric acid, and 10 at. water ; it dissolves with difficulty in water, unless converted into a neutral or acid salt ; hence the addition of dilute acid. The soda abstracts all the acid, the quinine precipitating as a hydrate.

Potash and ammonia are not so applicable to the precipitation of quinine, as both of them dissolve it, although in small proportions.

Properties.—Quinine obtained by precipitation is a snow-white crystalline powder, odourless, and of

a very bitter taste. It colours moistened litmus paper brown. Heated it fuses, loses its water, and on cooling solidifies to a resinous transparent mass; at a higher temperature it becomes black and burns completely, leaving no residue. Water dissolves only traces of it; strong alcohol dissolves it easily, and ether takes up $\frac{1}{60}$; the solutions have an alkaline reaction. Dilute acids dissolve it with the greatest readiness. Its behaviour with chlorine and ammonia is very characteristic: on rubbing pure quinine with chlorine water, and then adding caustic ammonia, a dark grass-green flocculent precipitate results. From its high price it is frequently adulterated. *Cinchonine* is present if the residue, on exhaustion with ether, readily dissolves in alcohol or dilute acids, forming a very bitter solution. If the residue is not soluble in dilute acids, several substances may be present; *gypsum*, if a residue on heating dissolves in a large quantity of water; *phosphate of lime*, when it is soluble only in nitric or hydrochloric acids; *chalk*, if these give an effervescence and dissolve; *starch*, when iodine causes a blue colour in it; and so on. (*Vide* QUIN. SULPH.)

QUININUM SULPHURICUM.

Quinæ Disulphas.—Disulphate of Quinine.

FORMULA: +

$$2C_{20}H_{12}NO_2 + SO_3 + 10HO = 2Q + SO_3 + 10HO.$$

Preparation. — 50 Parts of coarsely-powdered yellow bark * are digested in a leaden vessel with

* The residue from aqueous infusions contain most of the quinine, and may be advantageously employed by pharmaceutists. A quantity less than 10 pounds should never be operated on. Of fresh bark, the decorticated is to be chosen, as the interior portion (falsely termed the alburnum), is the chief seat of the alkaloid.

200 parts of water, in which 1 part of concentrated sulphuric acid has previously been mixed, for one day, at a gentle heat, strained in a linen bag, the residue strongly pressed, treated a second time, with 150 parts of water and $\frac{2}{3}$ part of sulphuric acid, and a third time, with 150 parts of pure water. The liquids are boiled in the same vessel to 50 parts, allowed to rest quietly for some days, filtered, and supersaturated with caustic soda solution. When the soda solution no longer causes a turbidness, the precipitate is allowed to subside, collected on a filter, washed with cold water, and dried. The dried mass is finely powdered, digested with 10 times its weight of alcohol of 90 per ct., with a gentle heat for 1 day, filtered, and the residue well washed with alcohol; sufficient sulphuric acid is now added to give a faintly acid reaction to the alcoholic solution, then one-fourth its weight of water and the alcohol distilled off. The residual aqueous solution, which contains a mass of fine crystals, is poured into a porcelain dish, and the retort rinsed with water; the dish is warmed on a sand bath as long as its contents smell of alcohol; it is then placed in the cool for some days, the crystalline mass thrown on a cloth, and the coloured liquor removed by pressure. The yellow crystals are formed into a magma with water, again pressed, warmed with a large quantity of water, and caustic soda solution added until a strong alkaline reaction is obtained; after digesting some hours, the yellow precipitate is thrown on a filter, washed, dried, dissolved in alcohol of 90 per ct., the solution filtered, sulphuric acid added as before, then water, and the spirit distilled off, the residual mass freed from mother liquor by pressure, and dried. If not yet white the same treatment, with caustic soda, &c., must be repeated, when it will be obtained quite pure.

The yield varies, ranging between 1 and 3 per ct. of the bark used.

In general the alkaloid is thrown down with lime instead of soda, when of course hydrochloric acid must be substituted for sulphuric; this entails a slight loss, the quinine being somewhat soluble in lime water as well as in caustic potash and ammonia; soda possesses the advantage of abstracting the colouring matter better than the other alkalies, and not dissolving any of the alkaloid.

Recapitulation.—Quinine, together with a little cinchonine is found in cinchona bark, combined with tannic acid; this compound is slightly soluble in boiling water, but readily so in dilute acids; the solutions yield to soda a precipitate of the alkaloids combined with some of the tannin (more or less decomposed) named quina red, the greater part of this latter substance remains in the alkaline solution. Strong alcohol takes up the alkaloid (together with the greater part of the adhering colouring matter), with which sulphuric acid forms a sulphate. After removing the alcohol, the greater part of the quinine (as a basic sulphate) crystallizes; the sulphate of cinchonine, with most of the colouring matter and a little sulphate of quinine, remains in the mother liquor. The further treatment, to effect the entire purification of the salt, requires no further explanation.

The mother liquors are mixed, treated with excess of soda, and the precipitation (impure quinine and cinchonine) reserved for the next preparation of quinine; or it is precipitated with caustic ammonia, the resinous mass (a combination of quina red, tannin, resin, &c.) well washed with water, dried and used as chinoidine.

Properties.—Pure sulphate of quinine is a white, light salt, consisting of fine needles, belonging to the oblique rhombic system. It is odourless, but of an

intensely bitter taste. Heated it readily fuses, giving off 8 at. of water and retaining 2 at.; at a higher temperature it becomes red and burns without a residue. In cold water it is but slightly soluble, requiring 740 parts, but dissolves in 30 parts of boiling water. The solutions have a neutral reaction. A slight addition of acid assists its solubility in water to a great degree. In alcohol it is much more soluble; ether takes up very little of it. In commerce it is often found impure and adulterated. *Cinchonine* is known by shaking with 5 parts of water and 1 part of ammonia, filtering, washing the precipitate and agitating it with ether, when this alkaloid will cause the solution to be turbid. By ammonia the salt is decomposed, quinine and cinchonine are thrown down, the former being soluble, the latter insoluble in ether; the precipitate must of course be first freed by washing, from the sulphate of ammonia formed, as this is also insoluble in ether. *Salicine* is detected by the blood-red solution it forms with cold concentrated sulphuric acid, with which *starch*, *sugar*, *stearine*, or other organic matters are on the other hand coloured brown or black. Sugar imparts a sweet taste to water; starch and stearine remain dissolved by dilute sulphuric acid, the former gives a blue colour with iodine, the latter fuses to an oil in hot water. *Gypsum*, *chalk*, and *phosphate* of *lime* are known by their insolubility in alcohol, and not being affected on heating. *Borax* also remains on heating the salt to redness, and forms with alcohol a solution burning with a green flame.

QUININUM TANNICUM.

Tannate of Quinine.

FORMULA: $+$
$C_{20}H_{12}NO_2 + 2C_{18}H_8O_{12} = Q + 2\overline{T}a.$

Preparation.—2 Parts of sulphate of quinine are rubbed with 48 parts of distilled water, dilute sulphuric acid is added by drops until the salt is dissolved, and an aqueous solution of tannin added as long as a precipitate is formed. 4 Parts of tannin will be sufficient. The precipitate is thrown on a filter, washed with water until the liquor passing off has only a feeble acid reaction, then dried with a gentle heat. Its weight will equal 5 parts.

Recapitulation.—Tannin forms with quinine an insoluble bi-salt:—

$+$
1 at. $2Q + SO_3 + 10HO$ and 4 at. $\overline{T}a$, form
$+$
2 at. $Q + 2\overline{T}a$, 1 at. SO_3, and 10 at. HO.

5675 Parts of sulphate of quinine require therefore 10,600 parts of tannin. The washing must be discontinued when the liquor passing through the filter is only slightly acid, otherwise from the salt being somewhat soluble a loss will occur.

Properties.—Tannate of quinine is a yellowish-white and (when magnified) crystalline powder, possessing at first an astringent, afterwards a permanent bitter taste. When heated it fuses, becomes brown, carbonizes, and finally burns without a residue. 1 Part dissolves in 453 of cold and 21 parts of hot water; the solution is colourless, of a feebly acid reaction and an astringent bitter taste. Cold alcohol of 80 per ct. forms with $\frac{1}{30}$ its weight of tannate of quinine a pale straw-coloured solution; hot alcohol dissolves half its weight. Dilute sulphuric acid in the cold has scarcely any action on tannate of quinine, but on warming the quinine dissolves in

the sulphuric acid, the tannin separating and quickly disappearing; on cooling the tannin and quinine again combined, form a yellowish precipitate.

QUININUM VALERIANICUM.

Valerianate of Quinine.

FORMULA:

$$2C_{20}H_{12}NO_2 + C_{10}H_9O_3 + 4HO + 20Aq = \overset{+}{Q_2}\overline{V}a + 4HO + 20Aq.$$

Preparation.—1 Part of pure valerianic acid (the terhydrate) is dissolved in a flask with 180 parts of water, 3 parts of pure quinine added, (when recently precipitated and moist it dissolves most readily,) heated nearly to boiling, filtered whilst hot, and the filtrate placed in the cold. After some days the crystals which form are separated from the mother liquor, the latter evaporated but at a temperature under 120° Fah., and the salt dried with a very gentle heat. The yield is about 5 parts.

Recapitulation.—Quinine, especially when recently precipitated, is readily taken up by valerianic acid to form a basic salt:—

$$2 \text{ at. } \overset{+}{Q} + 3HO \text{ and } 1 \text{ at. } \overline{V}a + 3HO, \text{ form}$$

$$1 \text{ at. } \overset{+}{Q_2} + \overline{V}a + 4HO, \text{ and } 5 \text{ at. } HO.$$

4725 Parts of hydrate of quinine require therefore 1500 parts of the terhydrated acid. Besides the 4 at. of water of hydration, the salt will take up 20 at. as water of crystallization; but it must be evaporated at as low a temperature as possible otherwise instead of crystals, the surface of the liquid and the sides of the dish become covered with oily beads of a greenish-grey colour, which are the hydrate of the salt (with 4 HO). These in the warm form a

resinous amorphous tough mass which can be drawn into threads, but cold they are very brittle, forming when rubbed a grayish-white powder. At first when the solution is not very concentrated, the salt containing 24 at. of water crystallizes without difficulty, but when more concentrated, it is only at a very moderate temperature that the formation of the hydrate can be avoided.

Properties.—Valerianate of quinine crystallizes in colourless rhombohedral tables of a mother-of-pearl-like lustre, or else in stellated groups of opaque needles, smelling slightly of valerianic acid, with a bitter taste afterwards reminding one of valerian. Warmed it becomes tough, readily fuses to a colourless liquid, and giving off water is converted into the above named hydrate. Heated more strongly it gives off white vapours, ignites and burns without leaving a residue. 1 Part of the crystallized salt dissolves in 110 parts of cold and 40 parts of boiling water; in 6 parts of cold and in an equal weight of boiling alcohol of 80 per ct.; in ether it is readily soluble; the solutions have a neutral reaction. Water takes up scarcely $\frac{1}{1000}$ of the hydrated salt, yet it acquires from it a very bitter taste. Alcohol and ether act as readily on it as on the crystallized. Adulterations may be detected like those under the article QUIN. SULPH.

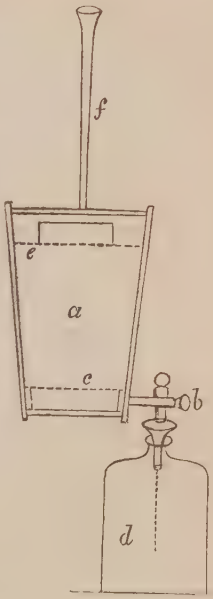
RESINA JALAPÆ.

Resin of Jalap.

FORMULA: $C_{42}H_{35}O_{20}$.

Preparation.—1 Part of coarsely powdered jalap root (Ipomœa Schiedeana) is digested with 2 parts of alcohol from 70 to 80 per ct. for 2 days in a copper still, the alcohol allowed to boil for some little time, and the heat continued until about $\frac{1}{10}$ has

distilled over. When thoroughly cool (about the third day) the contents of the still are placed in an apparatus arranged as in the accompanying cut; *a.* is an oaken vat, in the side of which, and close to the bottom, is a cock, *b.*; *c.* is a false bottom, perforated with holes, and supported by four pegs about 2 inches long; it is covered with a piece of coarse flannel, on which the digested mass is placed; the spirit that has distilled over is then rinsed round the still, and poured on it, another perforated disk (*e.*) is now placed on the top, well pressed down with a stone, and the vat closed perfectly with a cover, in the centre of which is fitted air-tight a tin plate funnel tube (*f*), several feet long; the cracks between the cover and the vat are luted with clay. As soon as the alcoholic liquid has escaped by the tap, a fresh supply of alcohol is added through the funnel, and this is repeated until what passes off has but little colour, and gives no turbidness with water. The tinctures are then returned to the still, water $\frac{1}{3}$ the weight of the root employed



added, and the whole of the alcohol drawn over. The still is allowed one day to cool, the hardened resin is then separated from the brown aqueous liquid, and placed in a copper vessel, washed several times with hot water, and evaporated, stirring constantly with a wooden spatula, until a small portion withdrawn becomes brittle on cooling. The average yield is from 12 to 14 per ct. of the weight of the root.

To get back the alcohol which remains in the root, the latter is washed, in the same vessel, with water as long as the liquor which runs off tastes of spirit, this is then distilled.

If several quantities are digested one after the other, a saving of spirit is effected by distilling only the first saturated tinctures with water, and using the last more dilute ones for exhausting and washing a fresh portion of root.

The method very often recommended, of treating the root with water previous to digesting with alcohol, in order to obtain a larger yield and a paler resin, I have not found to succeed. It entails more labour, the resin is no paler, and the product, instead of being greater, is less in several experiments that I have made. This result is not strange, for although a jalap resin is quite insoluble in pure water, yet this menstruum takes up extractive, gummy, and saccharine matter from the root whilst the resin forms an emulsion in the solution, and is lost.

The fibrous, fusiform Jalap root (Ipomœa Orizabensis), which goes by the improper name of Jalap stalks, "Stipites Jalapæ," yields a resin scarcely distinguishable from that of the thick knotty root in appearance or medicinal effects, but differs somewhat in its chemical properties. The yield of resin is in general scarcely 6 per ct., sometimes as high as 9 per ct.; formerly, when it first became a commercial article, I have obtained as much as 11 or 12 per ct. The reason of this considerable differ-

ence is owing, I suspect, to less care being taken in separating the worthless roots.

Recapitulation.—Jalap resin exists in an uncombined state in the roots, and is taken up by alcohol, together with other matters (saccharine and extractive). To facilitate the extraction, the root is powdered, but not too finely, or the passage of the spirit through it will be too much impeded. With the apparatus previously described, the whole of the resin may be washed out from the digested mass with less waste of alcohol than in digesting and expressing several times. By adding water to the tincture all the alcohol may be distilled from it without any fear of the resin becoming burnt; another advantage is that the water retains in solution the saccharine, extractive, and all other matters soluble in it, which with the resin were taken up by the alcohol; and this solution, which is of a deep brown colour, and has a faintly sweet taste, may be thrown away, as it yields but traces of resin in evaporating to dryness, and redissolving. To remove the extractive matter which still adheres to it, the resin is washed several times with warm water, and then warmed over the fire until the water with which it is combined (about $\frac{1}{3}$ its own weight) is evaporated.

Properties.—Jalap resin thus prepared is a brownish brittle mass, externally dull, and pulverulent, internally shining, and readily broken, possessing the repulsive smell of jalap, and a somewhat pungent taste. It forms a yellowish-gray powder. Its colour is due to some matter, removable by digestion with animal charcoal, which treatment for medicinal purposes is superfluous. When warmed, it fuses, giving off its peculiar odour in a high degree; heated more strongly, it ignites, and is completely consumed. Water does not dissolve it. In alcohol it is readily soluble, giving a neutral reaction. Ether abstracts $\frac{1}{5}$ the weight of the resin,

whilst that prepared from the fusiform root is entirely soluble in this menstruum. The portion of the resin of the knotty root dissolved by ether is a soft resin; the insoluble portion has the composition given at the commencement of this article; the resin of the fusiform root is simple, and consists of $C_{42}H_{34}O_{18}$. It dissolves in caustic potash and soda, also in acetic acid, but is insoluble in fatty and ethereal oils. The commercial is often adulterated with *Colophony* and *Guaiacum resin*. These two substances dissolve in oil of turpentine, resin of jalap does not; if, therefore, the turpentine solution gives a resinous residue on evaporation, this adulteration is evident. Without care, however, this test may prove false, as old oil of turpentine yields a resin on evaporation, if, therefore, one has occurred, the oil of turpentine must be freshly distilled and again digested. To determine whether the residue is guaiacum or colophony, the resin is dissolved in alcohol and the solution divided; to one portion about twice its volume of water is added, and then, by drops, just enough pure caustic potash solution to render the milky solution clear; if after adding some drops it still remains turbid colophony is certainly present and possibly guaiacum resin; this is detected by adding to the other portion of the spirituous solution a few drops of solution of perchloride of iron; if no change occurs guaiacum is absent whilst a deep blue solution quickly becoming green indicates its presence; solution of chloride of lime, nitrous acid or acid spirits of nitric ether may be substituted for perchloride of iron. The blue colour arises from the oxidation of the resin by the above-named substances.

SALICINUM.

Salicine.

FORMULA: $C_{26}H_{18}O_{14}$.

Preparation.—20 Parts of dried or 50 parts of fresh willow bark (from the Salix pentandra, alba, fragilis, purpurea, vitellina, or helix) is shredded and digested in a copper vessel for one day at a gentle heat, with 100 parts of water in which 2 parts of hydrate of lime have been previously mixed, the whole is then boiled for one hour, being well stirred, then strained and pressed. The residue is again treated with 60 parts of water and 1 part of hydrate of lime. The liquids are allowed to deposit, then returned to the cleaned copper, about 2 parts of fresh bullock's blood added and boiled a short time, then strained and the clear liquid evaporated over a naked fire. When it acquires the consistence of a thin syrup, 5 parts of freshly heated and powdered wood charcoal are added, and the whole evaporated with constant stirring, in a sand or water bath to dryness, or until the mass is crumbling and then dried at a low temperature. The dry mass is finely powdered, mixed in a flask or still according to quantity, with 4 times its weight of alcohol of 80 per ct. digested for some hours with a gentle heat, filtered and the residue twice again treated with twice its weight of alcohol of 80 per ct. The tinctures are mixed and $\frac{1}{6}$ their weight of water added, then distilled and the residual fluid placed in a porcelain dish in a cool place for some days. The crystalline mass which now separates is freed by straining and pressing from the adhering liquor; this on again evaporating yields fresh crops of crystals; these require to be thoroughly well pressed each time. The last portion of mother liquor is

evaporated to an extract and reserved for the next preparation of salicine.

The crystals of salicine are dried, mixed with four times their weight of water, and then treated with their own weight of animal charcoal, (which has been digested with hydrochloric acid well washed and heated to redness,) the whole digested for some hours at a gentle temperature, filtered, the residue washed and the liquid slowly evaporated, when pure white crystals will form and only the last portions of mother liquor will yield yellow ones; if in sufficient quantity, these and the residual mother liquor are again treated with animal charcoal. The product of pure salicine will be about 1½ or 2 per ct. the weight of dry bark.

Recapitulation.—Salicine exists in a free state in the bark of most if not all species of Salix (and Populus); but in some the quantity is too small to be worth employing. Those mentioned at the commencement of this article are especially rich in it, as may be known by the red colour which concentrated sulphuric acid strikes when rubbed on the inner surface of their fresh bark. Water extracts from the bark, besides salicine, a large quantity of extractive matter, gum, and tannin which latter strikes a green colour with salts of iron; the last and also a portion of the two other substances are precipitated by the lime. The solution does not become quite clear on standing; bullock's blood, from the albumen it contains readily effects this when boiled with it. The extract must be deprived as much as possible of its water before treating with spirit, and would require a long time to effect it but for the charcoal, and this also removes a portion of the colouring matter. Alcohol extracts the salicine and a certain portion of colouring extractive matter. By crystallization, the latter is mostly separated, but on treating with animal charcoal it is entirely removed.

Properties.—Pure salicine forms small white brilliant needles and plates which are odourless and of a very bitter taste. Heated it fuses, at a higher temperature it decomposes, giving off empyreumatic products having an acid reaction, and burns without a residue. In water and alcohol it is readily soluble. Cold water dissolves $\frac{1}{22}$, boiling water more than twice its weight; cold alcohol 80 per ct. dissolves $\frac{1}{30}$ boiling $\frac{1}{3}$ its weight; the solutions do not affect vegetable colours. By ether it is unacted on. With concentrated sulphuric acid it acquires a red colour, and on treating the mixture with water a red powder precipitates containing sulphuric acid, and to which the name of Rutilin has been given. Its purity may be readily judged of by these properties.

SANTONINUM.

Santonine.

FORMULA: C_5H_3O.

Preparation.—8 Parts of coarsely powdered wormseed are digested with 3 parts of hydrate of lime and 32 parts of alcohol of 40 per ct. in a copper still for one day, strained and pressed, then twice again digested with the same amount of alcohol. The mixed tinctures are distilled until the residue equals 24 parts. The latter is filtered, the filtrate evaporated to half, acetic acid added in slight excess, and allowed to remain some days undisturbed. The crystalline mass is thrown on a funnel loosely stopped, washed with cold water, dried, boiled with ten times its weight of alcohol of 80 per ct., the solution digested some hours with animal charcoal, filtered whilst hot, and the charcoal washed with hot alcohol; the solution is allowed to crystallize and the mother liquor evapora-

ted to fresh crystallization. The crystals are dried and kept excluded from the light. The yield from 8 pounds of wormseeds is from 2 to 2½ ounces.

The brown liquor which separates from the first crystals formed contains a small amount of santonine, but not enough to be worth separating.

Instead of fresh wormseeds, those from which the ethereal oil has been distilled may be employed. The residual mass is weighed, to determine the amount of water it contains; alcohol of 80 per ct. to equal in weight the water, is added, and hydrate of lime, ⅜ the weight of the seed; then proceed as above.

Recapitulation.—In wormseed the santonine is uncombined; to abstract it easily, its property of forming, with lime, a compound readily soluble in water or dilute alcohol, but not in strong alcohol, is taken advantage of. Dilute alcohol is preferred to water, as taking up less of the extractive matter. When the alcohol is removed, the santonine is entirely precipitated on treating with acetic acid, which takes the lime from it; an excess of acetic acid, as it would dissolve the santonine, must be avoided. The crystalline mass is first washed with cold water, to remove adhering extractive matter, then dissolved in alcohol, decolourized with animal charcoal, and crystallized. During crystallization, and afterwards, the light is carefully excluded from the pure santonine, otherwise it acquires a yellow colour; the chemical composition appears to be but slightly or not at all changed, for the yellow salt, dissolved in caustic potash and re-precipitated by acetic acid, yields white crystals.

Properties.—Pure santonine crystallizes in colourless, right rhombic, flattened prisms, is odourless, and only after remaining in the mouth some time a bitter taste is perceptible. Exposed to the air it remains unaltered, whilst light, on the other hand, as stated above, gives it a yellow colour, which in

direct sunlight requires only a few minutes. When heated it fuses, solidifying on cooling, without having undergone any change. Heated somewhat over its fusing point it sublimes, undecomposed, in dense white irritating vapours; if the temperature is raised still higher it gives off yellow vapours, which form an uncrystallizable sublimate, a product of decomposition; finally it carbonizes, leaving, when heated to redness for some little time, no more residue. Cold water dissolves but traces of santonine; hot water $\frac{1}{250}$; it readily dissolves in 43 parts of cold and 3 parts of boiling alcohol, of 80 per ct.; in 75 parts of cold and 42 parts of boiling ether; these solutions have a neutral reaction, and possess a pure intensely bitter taste. It also dissolves in fatty and ethereal oils; when not entirely pure, it possesses a faint smell and tastes of wormseed. It is sometimes adulterated with *gum arabic* and *borax*. Gum readily dissolves in cold water, and borax remains on heating to redness; alcohol shaken on the residue gives a green flame when ignited.

STANNUM CHLORATUM LIQUIDUM.

Stanni Protochloridum Liquidum. — Liquid Protochloride of Tin.—Hydrochlorate of Protoxide of Tin.

Formula: $SnCl + xHCl + xAq$.

Preparation.—1 Part of metallic tin, very finely rasped, is digested, at a gentle heat, in a flask with 4 parts of hydrochloric acid, spec. grav. 1·130, until no more action is perceptible on the metal, then diluted with water sufficient to bring it to 12 parts, filtered, and the filtrate kept, with a piece of tin, in a stoppered bottle.

Recapitulation.—Metallic tin dissolves in hydrochloric acid but slowly, though facilitated by a

gentle heat. The chlorine of the acid combines with the tin, the hydrogen is given off:—

1 at. Sn, and 1 at. HCl, form
1 at. SnCl, and 1 at. H.

725 Parts of tin require 455 parts of anhydrous, or 1750 parts of hydrochloric acid, spec. grav. 1·130; but, in order to retain it in solution, and also to allow for acid lost during digestion, the quantity of acid must be nearly doubled. The pure compound, SnCl, does not dissolve in water, but becomes decomposed into a basic salt, precipitating in white flocks, and an acid one, which remains in solution:—

3 at. SnCl, and 3 at. HO, form
1 at. SnCl + SnO + 2HO, and 1 at. SnCl + HCl.

In order to obtain a perfect solution with protochloride of tin, the water must first be mixed with a considerable portion of hydrochloric acid. If a slight portion of tin remains undissolved, it proves that no bichloride is present. The solution sometimes contains a black residue, from foreign metals, as arsenic, antimony, and (with excess of tin) copper, if present. Most of the antimony and arsenic will be carried off by the hydrogen, the action of which, however, a portion of these metals generally escapes, and, being insoluble in hydrochloric acid alone, is precipitated. The metallic tin in the solution preserves it as protochloride.

Properties.—Protochloride of tin, thus prepared, is a transparent solution, odourless, but of an acid, astringent, metallic taste. Evaporated it gives off hydrochloric acid and water, crystallizes as a neutral salt with 2 at. of water, = SnCl + 2HO, which is soluble in water containing a certain quantity of hydrochloric acid. In the air it decomposes gradually to a yellowish-white powder of hydrated oxide of tin and bichloride of tin:—

2 at. SnCl, 2 at O, and 1 at. HO, form
1 at. $SnCl_2$, and 1 at. $SnO_2 + HO$.

The addition of metallic tin prevents this decomposition, by which its use as a test for gold is destroyed. So long as it is only protochloride, a bluish-gray precipitate forms with solution of gold; if it contains some bichloride, the precipitate has more of a purple colour; if it is all become bichloride, no precipitate will occur. With the protosalts, or corresponding compounds of mercury, the protochloride of tin gives an immediate gray precipitate, this is metallic mercury very finely divided, whilst the solution contains perchloride of tin, or a corresponding salt of peroxide of tin; for instance,

2 at. SnCl, and 2 at. $Hg_2O + SO_3$, form
1 at. $SnCl_2$, 1 at. $SnO_2 + 2SO_3$, and 4 at. Hg.

If protonitrate of mercury has been used, the oxide of tin, forming no soluble compound with nitric acid, is precipitated as hydrate with the metallic mercury. Protochloride of tin causes, with persalts of mercury, on the other hand, at first a white precipitate of calomel (Hg_2Cl), which, on a further addition of the reagent, becomes gray from metallic mercury:—

1 at. SnCl, and 2 at. HgCl, form
1 at. $SnCl_2$, and 1 at. Hg_2Cl; further,
1 at. SnCl, and 1 at. Hg_2Cl, form
1 at. $SnCl_2$, and 2 at. Hg.

Tin of commerce generally contains impurities, which are partly found in the solution. *Arsenic* and *antimony* are detected most satisfactorily by Marsh's apparatus (*vide* Acid. Hydrochlor.). They will mostly be given off, during the solution of the metal, by hydrochloric acid, as, arseniuretted and antimoniuretted hydrogen; any portion which is not thus volatilized will form a blackish deposit in the liquid, and when washed, dried, and heated

on charcoal before the blowpipe, arsenic will be detected by the garlic odour, and antimony by the white deposit and metallic globules on the charcoal support. *Sulphur*, another frequent impurity in tin, is also evolved in combination with hydrogen. *Copper*, when pure, is insoluble in hydrochloric acid, but dissolves when oxidized by the action of air, and being taken up by excess of ammonia, in precipitating the protoxide of tin, imparts to the supernatant liquor a blue colour. *Iron* is discovered by the deep red colour with sulphocyanide of potassium, if the tin solution has been treated with aqua regia to convert the iron into chloride. If *lead* is present, and not in very small quantities, it crystallizes as chloride, in needles, from the tin solution; a smaller quantity is detected by a solution of sulphate of soda, which causes an almost insoluble precipitate of sulphate of lead.

STANNUM BICHLORATUM.

Stanni Perchloridum.—Spiritus Fumans Libavii.—Bichloride of Tin.

Formula: $SnCl_2$.

Preparation.—An amalgam of 4 parts tin and 1 part mercury, obtained by fusing the tin in warmed mercury, is finely powdered, and placed, with 19 parts of bichloride of mercury (granulated), in a retort, which has been warmed to expel all moisture, large enough to hold twenty times the quantity, and distilled, at first with a gentle heat, until no more white fumes pass over. The receiver must be well cooled during the operation. The distillate to be kept in a stoppered bottle. Its weight equals 10 parts.

Recapitulation.—When metallic tin and bichloride of mercury, in proper proportions, are heated, the

tin abstracts all the chlorine from the mercury, forming the readily-volatile bichloride of tin, which condenses in the receiver to a thick fluid, metallic mercury forming the residue :—

1 at. Sn, and 2 at. HgCl, form
1 at. $SnCl_2$, and 2 at. Hg.

725 Parts of tin require 3386 parts of bichloride of mercury, or 4 parts require nearly 19 parts. The use of the metallic mercury is simply to allow the tin to be finely divided. The chloride of mercury must neither be very finely powdered nor intimately mixed with the tin amalgam, otherwise the commencement of the action, even at a very gentle heat, is accompanied with an explosion powerful enough to project a portion into the receiver and spoil the results. In consequence of this explosion, in a greater or less degree, a white deposit always covers the upper sides of the retort, it consists of protochloride of mercury and tin, amongst which will be found globules of mercury ; but as the heat throughout the experiment is not high enough to effect the sublimation of these products, the distillate remains uncontaminated ; their formation is thus explained :—The bichloride of mercury does not at once lose all its chlorine, or the tin at once form bichloride, but first becomes protochloride and gradually bichloride. If the retort is not previously well dried, its neck will contain a crystalline deposit of hydrated chloride of tin, $=SnCl_2 + 2HO$.

Properties.—Anhydrous bichloride of tin is a colourless clear liquid spec. grav. 2·28, of a repulsive powerful odour, and an excessively corrosive astringent taste. In the air it forms dense white fumes from its combination with aqueous vapours to hydrated crystalline bichloride ; the addition of $\frac{1}{7}$ its weight of water entirely converts it into this compound, which in a large quantity of water is

readily and completely soluble. Its behaviour when heated is explained in its formation; its boiling point is 248° Fah. The dilute solution must undergo no change with bichloride of mercury or gold. (*Vide* previous preparation).

STIBIUM CHLORATUM LIQUIDUM.

Liquor Stibii Muriatici.—Antimonii Chloridum.—Liquid Chloride of Antimony.—Butter of Antimony.

FORMULA: $Sb_2Cl_3 + xHCl + xAq$.

Preparation.—2 Parts of commercial sulphuret of antimony powdered, are placed in a capacious flask, gradually treated with 8 parts of hydrochloric acid, spec. grav. 1·130, the flask placed on a sand-bath, and when all action ceases, 1 part of nitric acid, spec. grav. 1·20 added, the whole digested as long as yellowish-brown vapours are given off and then allowed to cool. The liquid is filtered, when it should weigh about 9 parts, poured into a retort, distilled in a sand-bath at a gentle heat, below that of boiling water, until the liquid passing over gives when dropped into pure water a white precipitate; the retort is now removed from the fire and its contents as soon as sufficiently cooled placed in a stoppered bottle. The product should be 6 parts of spec. grav. 1·530.

The preparation, though sufficiently pure as an external application, still contains all the impurities of the sulphuret of antimony; these may be got rid of by distillation, and if required pure, instead of removing the retort at the point above named the receiver is simply changed and the distillation continued (for this a naked fire is best) until the residue is dry. The neck of the retort is warmed, to fuse the solid portion contained in it, and the contents of

the receiver poured into a stoppered bottle. The spec. grav. is 1·40, less than that of the common chloride, the reason is the absence of the foreign bodies and unavoidable loss of a portion of chloride of antimony, to obtain the last portions of which, the heat must be so much increased as to volatilize portions of the chloride of iron, &c., and contaminate the distillate. By changing the receiver, products gradually becoming more concentrated may be obtained.

Recapitulation.—Sulphuret of antimony dissolves in hydrochloric acid with the evolution of sulphuretted hydrogen, and formation of chloride of antimony :—

1 at. Sb_2S_3 and 3 at. HCl, form
1 at. Sb_2Cl_3 and 3 at. HS.

2212 Parts of black sulphuret of antimony are decomposed into chloride of antimony and sulphuretted hydrogen by 1365 parts of anhydrous or 5250 parts of hydrochloric acid spec. grav. 1·130. In order to obtain a solution the acid must be in considerable excess, thus forming an acid salt, which to a certain extent is soluble in pure water, whilst the neutral salt is instantly decomposed. At first the action of the acid is violent and has consequently to be added gradually, but afterwards it almost entirely ceases, from the dilution of the acid by the chloride of antimony formed. A very considerable excess of hydrochloric acid would of course dissolve the sulphuret of antimony, but it is more convenient to effect it by the addition of a small portion of nitric acid ; aqua regia (or chlorine and nitric oxide) is formed from the hydrochloric acid present ; chlorine replaces the sulphur which precipitates, and nitric oxide $=NO_2$ is given off, forming brown vapours of hyponitric acid. As towards the end of the process, the fluid generally boils up considerably, the retort must be twice as large as would

otherwise be necessary. The reaction is thus expressed:—

2 at. Sb_2S_3, 6 at. HCl, and 2 at. NO_5, form
2 at. Sb_2Cl_3, 6 at. S, 6 at. HO, and 2 at. NO_2.

The other metals present (as iron, copper, lead, or arsenic) also dissolve, and from the action of the nitric acid on the sulphur a little sulphuric acid forms, which immediately passes to the lead; the filtered residue contains sulphur with traces of sulphate of lead and metallic sulphurets, also chloride of lead if much metallic lead were present. The filter must not be washed, otherwise the chloride of antimony will be decomposed. Warmed in a retort, the yellow filtrate only gives off at first hydrochloric acid, water, and any chloride of arsenic that may be present, and if the receiver is changed, without discontinuing the process, when $\frac{1}{3}$ of the solution has passed over, no loss of chloride of antimony will occur. Lastly, the chloride of antimony (as an acid compound) passes over, collecting in the receiver as a colourless liquid; the proportion of chloride in this gradually increases, until at last, the compound free from acid and water condenses, in the cold neck of the retort, to the consistence of butter; on warming it again liquifies and flows into the receiver. The retort will contain any chloride of lead, chloride of iron, and chloride of copper; whilst the chloride of arsenic will be found in the first third of the distillate.

The name of butter of antimony was, from its consistence, formerly given to the preparation obtained by the dry distillation of antimony or sulphuret of antimony and bichloride of mercury. In the first case pure mercury (partly as calomel), in the second, sulphuret of mercury, remains in the retort; for

2 at. Sb and 3 at. HgCl, form
1 at. Sb_2Cl_3 and 3 at. Hg.; or
2 at. Sb. and 6 at. HgCl, form
1 at. Sb_2Cl_3 and 3 at. $Hg_2Cl.$; further,
1 at. Sb_2S_3 and 3 at. HgCl, form
1 at. Sb_2Cl_3 and 3 at. HgS.

Properties.—As first prepared, chloride of antimony is a dark yellow liquid, (from chloride of iron,) when rectified it is colourless, of spec. grav. 1·4, fumes in the air, has a sharp acid odour and corrosive taste. Its chief characteristic is the formation of a milky liquid when mixed with water; a small quantity of water effects no perceptible change, as it is increased a white precipitate is seen to form, the chloride separating into a basic insoluble compound (chloride of antimony with hydrated oxide of antimony) and an acid salt (chloride of antimony with hydrochloric acid); lastly, this acid salt undergoes decomposition, and when water no longer causes a precipitate, the supernatant liquid will be found to contain scarcely any antimony which now exists in the precipitate as a very basic salt, consisting of from 9—10 per ct. chloride of antimony, and 90—91 per ct. of hydrated oxide of antimony.* The supernatant liquor besides traces of antimony will contain all foreign metals present in the sulphuret of antimony (iron, copper, lead, &c.). Tartaric acid prevents a precipitation of chloride of antimony in water; or, what is the same thing, dissolves the precipitate formed; if, therefore, a considerable proportion of tartaric acid is added to the chloride, the *iron* present may be detected by sulphocyanide of potassium, and the *lead* by sulphate of soda. *Copper* is known by the blue colour of the liquid on supersaturating with ammonia; if the blue colour is not

* Precipitates I obtained in three separate experiments by treating the butter of antimony with excess of water, yielded 9·0, 9·2, and 10·2 per ct. of chloride of antimony, which corresponds to the formula $13(Sb_2O_3 + HO) + Sb_2Cl_3$.

sufficiently evident, a part of the solution is to be supersaturated with acetic acid and ferrocyanide of potassium added, which, if copper is present, will cause a chocolate precipitate; the other portion is supersaturated with hydrochloric acid, treated with sulphuretted hydrogen and the precipitate, if it is not yellow, is shaken with ammonia and tested for arsenic as described under the article, KALIUM OXYD. TART. STIB.

STIBIUM OXIDATUM.

Antimonii Oxidum.—Oxide of Antimony.

FORMULA: $Sb_2O_3 + HO$.

Preparation.—(*a.*) *From sulphuret of antimony.* 12 Parts of commercial sulphuret of antimony are dissolved as in the foregoing article in 48 parts of common hydrochloric acid and 6 parts of nitric acid, the solution diluted with as much water as it will bear without becoming milky (about 24 parts) is filtered, the clear solution agitated in an earthen, or in large quantities in a wooden vessel containing 400 parts of pure water, and the whole well shaken together; if after its subsiding, water no longer causes a precipitate in the supernatant liquid (50—100 parts of water must be employed) it is poured off, the precipitate washed by decantation as long as it retains its acid reaction and sulphocyanide of potassium causes a reddening in the wash-water. The white pulpy mass, thoroughly washed, is then placed in a porcelain dish, warmed, 2 parts of finely powdered crystals of carbonate of soda gradually added, digested for 1 or 2 hours, and the precipitate washed as before with pure water until nitrate of silver causes no change in the wash-water; it is then collected on a linen strainer, pressed and dried with

a gentle heat. About 9 parts of oxide of antimony will be the result.

(*b.*) *From metallic antimony.* 3 Parts of finely powdered metallic antimony are treated in a capacious porcelain dish with 7 parts of concentrated sulphuric acid, warmed over a gentle fire, with constant stirring until dry, the mass moistened with water, then poured into a good quantity (about 100 parts) of water; now washed as under (*a.*), digested at a gentle heat with crystallized carbonate of soda, which is added as long as it causes an effervescence, ($2\frac{3}{4}$ parts of soda will be sufficient) washed and dried at a gentle heat. The yield is about $3\frac{1}{2}$ parts.

These two are the best and cheapest methods of making the oxides of antimony; the first is the most convenient in practice, and yields the purest product.

Recapitulation.—(*a.*) Under the article STIB. CHLOR. the process of dissolving the sulphuret of antimony and precipitating with water is sufficiently explained. When the solution no longer yields a precipitate, the latter will contain about 10 per ct. of chloride of antimony or 90 per ct. of hydrated oxide, agreeing with the formula $13(Sb_2O_3 + HO) + Sb_2Cl_3$. On treating commercial sulphuret of antimony with hydrochloric acid containing nitric, most of its impurities, as sulphurets of arsenic, copper, lead, and iron, are converted into chlorides which dissolve in water without becoming again precipitated, unlike chloride of antimony, so that they are entirely removed by washing. The antimony is so thoroughly precipitated that only $\frac{1}{60}$ dissolves in the acid wash-water, and becomes lost. None but distilled water must be used in the process, as the sulphates in well water would convert the chloride of lead, which though not very soluble, is entirely so in pure water, into insoluble sulphate of lead and thus contaminate the precipitate of antimony. By the action of the nitric acid on the sul-

phur a little sulphuric acid is formed which combines with the lead; the quantity thus thrown down is however very minute; if the hydrochloric acid is not free from sulphuric, the sulphate of lead of course increases in proportion; if, however, the solution from sulphuret of antimony is treated, previous to its filtration, with just so much water that it is not rendered milky, the sulphate of lead which is slightly soluble in strong acid solutions is thrown down and remains on the filter.

The Algaroth's powder obtained from 12 parts of common sulphuret is generally 9 parts. It must not be dried previously to treating with soda, otherwise having acquired a more dense consistence, the action of the alkali will be hindered. Warmed in contact with this pulpy mass, the carbonate of soda gives off its acid with effervescence, the sodium combines with the chlorine of the chloride of antimony in the Algaroth's powder, and the antimony uniting with the oxygen falls in combination with 1 at. of water, as hydrated oxide of antimony:

1 at. $13(Sb_2O_3 + HO) + Sb_2Cl_3$, and 3 at. $NaO + CO_2 + 10HO$, form

14 at. $Sb_2O_3 + HO$, 3 at. NaCl, 3 at. CO_2, and 9 at. HO.

29260 Parts of Algaroth's powder require 5370 parts of carbonate of soda, and as 29260 parts of the former correspond to about 39000 parts of sulphuret of antimony, 12 parts of sulphuret of antimony should require only $1\frac{3}{4}$ parts of soda, but a slight excess of the latter is requisite, as the supernatant liquor must possess an alkaline reaction, to insure the complete decomposition of the chloride of antimony; on the other hand, a large excess of carbonate of soda must be avoided, as this has a slight solvent power over the precipitate.

(*b.*) Metallic antimony is unacted on by dilute sulphuric acid, or by concentrated when cold; the

latter acid when hot dissolves it, one portion giving up a part of its oxygen, with evolution of sulphurous acid, and the other portion dissolving the oxide formed :—

2 at. Sb, and 6 at. SO_3, form
1 at. $Sb_2O_3 + 3SO_3$, and 3 at. SO_2.

1612 Parts of antimony require 3678 of hydrated sulphuric acid, or 3 parts nearly 7 parts. To facilitate the action of the acid, the metal must be very finely divided, and the mass well stirred ; in spite of this, a part of the metal remains unacted on, the dry mass exhibiting a gray colour instead of white. A large amount of water changes the sulphate of antimony into free sulphuric acid, containing traces of oxide of antimony, and an insoluble basic sulphate. This is not so basic as the Algaroth's powder, as it contains only 7 at. of oxide of antimony to 2 at. of neutral sulphate, so that by treating with water only 21 at. of sulphuric acid are set free :—

9 at. $Sb_2O_3 + 3SO_3$, and xHO, form
1 at. $7(Sb_2O_3 + HO) + 2(Sb_2O_3 + 3SO_3)$, and 21 at. $SO_3 + xHO$.

After washing the mass with water, there remain 6 at. of sulphuric acid, which must be removed by 6 at. of soda :—

1 at. $7(Sb_2O_3 + HO) + 2(Sb_2O_3 + 3SO_3)$, and 6 at. $NaO + CO_2 + 10\ HO$, form
9 at. $Sb_2O_3 + HO$, 6 at. $NaO + SO_3$, 6 at. CO_2, and 58 at. HO.

20996 Parts of basic sulphate of antimony require 10740 parts of soda, and as 20996 of the former correspond to 14508 parts of antimony, so 3 parts of antimony require $2\frac{1}{3}$ parts of soda. For the reason given under (*a*), a slight excess of soda is used.

Properties.—Pure oxide of antimony is a white (if prepared from metallic antimony of a grayish tint), odourless, and tasteless powder. Heated in closed vessels, it loses its water, acquires a yellow colour, fuses and solidifies on cooling to a white mass; heated more strongly it completely volatilizes. Heated in the open air it becomes yellow, without fusing, but, acquiring oxygen, it is converted into antimonious acid $=Sb_2O_4$, which is permanent in the air, and on cooling again becomes white. Heated on charcoal it is readily reduced to the metallic state, but quickly oxidizes again, passing off in thick white vapours, which are deposited on the charcoal. Hydrochloric acid, especially when warm, readily dissolves it; water precipitates it from this solution as Algaroth's powder. Tartaric acid readily dissolves it, forming a compound entirely soluble in water. In both solutions sulphuretted hydrogen causes a dark orange-red precipitate. If it has a gray appearance *metallic antimony* is present, and the residue, insoluble in the above-named acids, has a metallic lustrous appearance. Should water, after shaking it with the preparation, leave a residue on evaporation, the latter has not been sufficiently washed. *Sulphuric, hydrochloric,* or *nitric acid* (from the use of a deficiency of soda) are detected by digestion, for half-an-hour, at a gentle heat, with a solution of pure carbonate of soda, filtering, acidifying with acetic acid and testing with chloride of barium, acetate of silver, and solution of indigo. Arsenious acid is also readily dissolved by a solution of soda, and the liquid acidified with hydrochloric acid gives a yellow precipitate with sulphuretted hydrogen; as this precipitate may possibly contain a little oxide of antimony (dissolved by the soda), the experiment is controlled by heating with oxalate of potash, as described under the article KALIUM OXID. TART. STIB. Nitric acid must take up nothing but a trace of

oxide of antimony; if the solution gives a red colour with sulphocyanide of potassium, *iron* is present; a blue one with excess of ammonia is due to *copper*; a white precipitate in the same solution, with sulphate of soda, arises from *lead*. Oxide of antimony prepared by digesting the metal with nitric acid, may possibly contain a *higher oxide of antimony* (antimonious or antimonic acid). To determine this, 3 parts of the oxide are mixed with 1 part of finely powdered sulphuret of antimony, the mixture shaken into a small flask, in the neck of which is fastened one end of a bent tube, the other end dipping into a diluted solution of caustic ammonia, the flask is heated over a spirit lamp until its contents become liquid, and retained for some minutes in this state. The ammoniacal solution is supersaturated with hydrochloric acid, and sulphuretted hydrogen passed into it; if the oxide was pure no change occurs, but if it contains antimonious or antimonic acid, a milkiness ensues. The theory is this: oxide of antimony fused with sulphuret of antimony forms the so-called "vitrum antimonii;" antimonic or antimonious acid yields the same compound, but at the same time 1 or 2 at. of oxygen must be given off, which converts a portion of the sulphuret of antimony into oxide, and sulphurous acid which is evolved:—

9 at. Sb_2O_4, and 1 at. Sb_2S_3, form
10 at. Sb_2O_3, and 3 at. SO_2; or,
9 at. Sb_2O_5, and 2 at. Sb_2S_3, form
11 at. Sb_2O_3, and 6 at. SO_2.

Sulphurous acid is taken up by the ammonia, again liberated by hydrochloric acid, and then decomposes with sulphuretted hydrogen into sulphur and water:—

1 at. SO_2, and 2 at. HS, form
3 at. S, and 2 at. HO.

STIBIUM SULPHURATUM AURANTIACUM.

Stibii Persulphidum.—Sulphur Auratum Antimonii.—Persulphuret of Antimony.—Orange Sulphuret of Antimony.—Golden Sulphuret of Antimony.

FORMULA: Sb_2S_5.

Preparation (*a*). — *From sulphuret of antimony* and *sulphuret of sodium.*—8 Parts of dried and powdered sulphate of soda are intimately mixed with 6 parts of finely powdered sulphuret of antimony, and 3 parts of finely powdered wood charcoal, the mixture well pressed into an earthen or black lead crucible, which should only be ¾ filled, the crucible covered, placed in a good wind furnace, and heated gradually. When the mass has become quietly fluid, the heat is continued another quarter-of an hour, then poured into an iron pot, and a well-fitted cover placed on it. On cooling the mass is coarsely powdered, and in the same pot the crucible, if any of the preparation adheres to it, is boiled in 30—40 parts of water, the pieces removed, and the powder added to the boiling liquid; to this 1½ parts of powdered sulphur are added, the boiling continued half-an-hour, and then filtered. The clear liquor is evaporated as quickly as possible in a porcelain dish, until a cooled portion gives signs of crystallization, filtered whilst hot, and allowed to stand for some days in a cool place, in a porcelain or glass vessel. The crystals which separate are collected on a funnel, when drained they are spread on filtering paper, and put into a well-closed bottle as soon as they are tolerably dry. The mother liquor is also evaporated, the last portions of it may be thrown away. The crystallized salt is now dissolved in 4 times its weight of water, the solution filtered, and diluted with 8—12 times its

volume of water in an earthen or wooden vessel, that should be only $\frac{2}{3}$ filled; with constant stirring, dilute sulphuric acid, *free from arsenic*, is now added until effervescence ceases, and the liquid acquires an acid reaction. 24—27 Parts of sulphuric acid will be necessary. The operation must be conducted in the open air, on account of the quantity of sulphuretted hydrogen evolved, the precipitate is washed by decantation, the latter part of the time with distilled water, then thrown into a bag, pressed, dried with a gentle heat and kept in the dark in a well-closed vessel. The weight of product will be $5\frac{1}{2}$ or 6 parts.

(*b*) *From sulphuret of antimony* and *sulphuret of calcium.*—3 Parts of hydrate of lime, 2 parts of powdered sulphuret of antimony, and $1\frac{1}{2}$ parts of powdered sulphur are placed, with 24 parts of water, in a cast-iron vessel, which it must only $\frac{2}{3}$ fill, heated with constant stirring to boiling, and continued at this temperature, after the liquid has acquired a dark brown colour, for $\frac{1}{4}$ of an hour, then filtered. The residue, drained as much as possible from the liquid, is boiled, well stirred with 24 parts of water, and filtered. When quite cold the clear liquors are diluted with 40—60 parts of water, and precipitated, as under (*a*), with hydrochloric acid, free from arsenic, and of spec. grav. 1·130, previously mixed with twice its weight of water. About 6 parts of acid, of the above strength, are requisite. The precipitate is washed, collected and dried, as under (*a*). To insure the absence of lime, the washing is continued until the wash water gives no turbidness with oxalate of ammonia. The product is equal to the preceding one: 2 parts of sulphuret of antimony yield 2 parts.

Recapitulation.—(*a*) On heating to redness a mixture of sulphate of soda, sulphuret of antimony, and carbon, the latter abstracts the oxygen of the

soda, evolving it as carbonic oxide (hence the frothing up of the mass), and the sulphuret of sodium (3 at.) combines with 1 at. of sulphuret of antimony to a sulphur salt, the hyposulphantimoniuret of sodium :—

3 at. $NaO + SO_3$, 1 at. Sb_2S_3, and 12 at. C, form 1 at. $3NaS + Sb_2S_3$, and 12 at. CO.

2670 Parts of anhydrous sulphate of soda require 2212 parts of sulphuret of antimony and 900 parts of carbon; the latter, from the impurities of wood charcoal, must be somewhat increased. The heat should not be continued longer than directed, otherwise the sulphuret is converted, by the oxygen of the air, into oxide of antimony, which the excess of carbon reduces to the metallic state. When the fused mass is boiled with water and excess of sulphur, the sulphuret of sodium undergoes no change, but the sulphuret of antimony, combining with more sulphur, is converted into persulphuret, $= Sb_2S_5$, and the composition of the salt is now $3NaS + Sb_2S_5$ (when crystallized, it equals $3NaS + Sb_2S_5 + 18HO$).

2212 Parts of sulphuret of antimony require 400 parts of sulphur. By crystallization the arsenic, which almost all commercial sulphuret of antimony contains, is removed, remaining in solution. Iron, copper, and lead remain as insoluble sulphurets on the filter. Dilute sulphuric acid decomposes the salt, and at the same time a portion of water; the sulphur of the sulphuret, combining with the hydrogen of the water, is given off, under effervescence, as sulphuretted hydrogen; the sodium and oxygen of the water form soda, which unites with the sulphuric acid, whilst the highest sulphuret of antimony precipitates, as such, in orange-coloured flakes :—

1 at. $3NaS + Sb_2S_5$, 3 at. SO_3, and 3 at. HO, form
3 at. $NaO + SO_3$, 3 at. HS, and 1 at. Sb_2S_5.

At first an insoluble, basic, pale yellow salt is formed, which is only decomposed completely by a considerable quantity (a slight excess) of acid. If we consider 2670 parts of sulphate of soda converted into sulphuret of sodium, and combined with a corresponding quantity of sulphuret of antimony, it will require 11034 parts of dilute sulphuric acid (1 part of conc. acid to 5 of water). This quantity of acid is never necessary, as a portion of the sulphur salt remaining in the mother liquor is lost, rather than run the risk of any contamination with arsenic. If the sulphuric acid contains arsenic, this metal, from the action of the sulphuretted hydrogen, is precipitated as a sulphuret with the antimony. From the effervescence on the escape of the sulphuretted hydrogen, the precipitating vessels must not be too small.

(*b*) When lime, sulphuret of antimony, and excess of sulphur are boiled in water, part of the lime yields up its oxygen to a part of the sulphur, forming hyposulphurous acid, which unites with the rest of the lime to hyposulphite of lime, $= CaO + S_2O_2$, and is readily soluble; the portion of calcium formed combines with an equivalent of sulphur, and the sulphuret of antimony, changed to a persulphuret, unites with the sulphuret of calcium, thus formed, to a soluble sulphur salt:—

9 at. CaO, 2 at. Sb_2S_3, and 16 at. S, form
2 at. $3CaS + Sb_2S_5$, and 3 at. $CaO + S_2O_2$.

4162 Parts of hydrate of lime ($CaO + HO$) require 4424 parts of sulphuret of antimony, and 3200 parts of sulphur. The lime, from the impurities it generally contains, must be considerably increased, an excess also not being detrimental. The propor-

tion of sulphur must not be increased, as, if more than 1½ parts are employed to 2 parts of sulphuret of antimony, free sulphuret of calcium is formed, which, if it contains more than 1 at. of sulphur, deposits the latter (*vide* SULPHUR. PRECIP.) when treated with an acid, and renders the preparation impure. The reaction commences with the boiling, and, being accompanied by effervescence, the vessel containing them must be sufficiently capacious. Of the impurities, iron, copper, and lead remain behind as sulphurets, together with excess of lime, and its contaminations; the arsenic passes into the filtered solution. In this process the arsenic cannot be removed by crystallization, the sulphuret of antimony and sulphuret of calcium crystallizing with difficulty, and being decomposed on evaporation. If the sulphuret of antimony contains arsenic, the latter will be found also in the golden sulphuret, which in this case is inapplicable as an internal remedy. Hydrochloric acid is decomposed with the dark yellow solution (which, if proper proportions have been employed, contains sulphuret of antimony and sulphuret of calcium, with hyposulphite of lime), its hydrogen, combining with the sulphur of the sulphuret of calcium, is given off as sulphuretted hydrogen; its chlorine forms, with the calcium, readily soluble chloride of calcium, and the highest sulphuret of antimony is thrown down:—

1 at. $3CaS + Sb_2S_5$, and 3 at. HCl, form
3 at. CaCl, 3 at. HS, and 1 at. Sb_2S_5.

The hydrochloric acid must contain neither sulphuric acid (otherwise gypsum precipitates) nor arsenic, as this becomes converted into sulphuret, and is thrown down. As soon as the precipitation is finished the supernatant liquid begins to acquire a turbidness. This arises from the decomposition of the hyposulphite of lime by the excess of hy-

drochloric acid, chloride of calcium and water being formed, and hyposulphurous acid liberated, which at the same moment separates into sulphur and sulphurous acid, 2 at. SO=1 at. SO_2, and 1 at. S.

When the sulphurous acid thus formed, comes in contact with sulphuretted hydrogen, portions of which are generally dissolved in the liquid, they are mutually decomposed into sulphur and water :—

1 at. SO_2, and 2 at. HS, form
3 at. S, and 2 at. HO.

For these reasons the supernatant liquid is to be poured off as quickly as possible. The action of the hydrochloric acid on the hyposulphite of lime is but slow in the dilute solution; and the latter is mostly removed undecomposed in the supernatant liquor; consequently the amount of free sulphur in the precipitate is trifling, and the odour of sulphuretted hydrogen, which the evolution of any quantity of sulphurous acid would instantly destroy, is removed from the solution only by repeated washing. The colour of the preparation will not be lighter from the admixture of sulphur, unless by using an excess of the latter, a higher sulphuret of calcium is formed on boiling, which on the addition of hydrochloric acid throws down sulphur (*vide supra*).

Properties.—Golden sulphuret of antimony is a soft, deep orange-coloured powder, (that prepared by *b* is somewhat paler), odourless and tasteless. It is unaltered in the air alone, but air and light decompose it, causing it to become paler. This change is due to the conversion of a portion of the sulphuret into oxide, by the oxygen of the air, and free sulphur :—

1 at. Sb_2S_5, and 3 at. O, form
1 at. Sb_2O_3, and 5 at. S.

I cannot state whether a portion of sulphur is at

the same time oxidized, my own experiments negative it. Heated in a narrow test tube it fuses, loses 2 at. of sulphur, and leaves a black liquid which cools to a crystalline mass, in appearance like Antimon. cruda. When this mass is heated it sublimes if air be entirely absent, but the slightest portion of the latter causes it to inflame; the sulphur burns to sulphurous acid, the antimony oxidizes, a small portion is given off in white vapours, but most of it remains as permanent antimonious acid. Dilute sulphuric nitric and hydrochloric acids have no action on the golden sulphuret. Concentrated hydrochloric acid dissolves it in the heat, sulphur being precipitated, and sulphuretted hydrogen given off:—

1 at. Sb_2S_3, and 3 at. HCl, form
1 at. Sb_2Cl_3, 2 at. S, and 3 at. HS.

The solution becomes milky with water (*vide* STIBIUM CHLOR.). The golden sulphuret dissolves readily and completely in caustic potash solution, undergoing a partial decomposition; sulphuret of potassium and antimonic acid being formed, the former of these combines with the rest of the sulphuret of antimony, the latter with the excess of potash:—

8 at. Sb_2S_3, and 18 at. KO, form
5 at. $3KS + Sb_2S_5$, and 3 at. $KO + Sb_2O_5$.

It is also slightly soluble in caustic ammonia, 1 part requiring 200 liquor ammonia, spec. grav. ·960. Should this leave a yellow powder *free sulphur* is present, but if it be a brown one, the golden sulphuret contains the *lowest sulphuret of antimony*, whilst a white one is probably *oxide* of *antimony*, which is detected by gently warming the golden sulphuret with solution of tartaric acid, filtering and treating with sulphuretted hydrogen, when a yellowish-red precipitate forms. Golden sulphuret of antimony should yield nothing soluble to water;

in the filtered solution *sulphuric acid* may be detected by nitrate of baryta; *hydrochloric acid* by nitrate of silver; *lime* by oxalate of ammonia; *magnesia* (after separating the lime) by phosphate of ammonia. Lime and magnesia may also be mixed with the precipitate combined with *carbonic acid;* in this case dilute nitric acid causes an effervescence, and in the filtered solution saturated with ammonia, both bases may be detected. If ammonia alone causes a precipitate in the nitric acid solution, *alumina* is present. *Silica* is detected by boiling the golden sulphuret with concentrated hydrochloric acid, filtering, washing with tartaric acid solution, then with water, drying and heating the residue in a platinum spoon, when a white powder insoluble in acids remains. On treating with hydrochloric acid the antimony is dissolved, the sulphur and silica separating. To free this residue completely from the antimony solution, it is treated with tartaric acid, as pure water again precipitates the antimony; by heating to redness the sulphur is evolved, and the silica remains. *Lead*, *iron*, and *copper* are detected as under "STIB. CHLOR." with sulphate of soda, sulphocyanide of potassium and ammonia. *Arsenic* is detected most certainly by the process given under the article TARTAR EMETIC; viz., by deflagrating with four times its weight of nitre, heating to redness for a quarter of an hour, softening the mass with water, supersaturating with dilute sulphuric acid, evaporating nearly to dryness, again treating with water, filtering and passing sulphuretted hydrogen into the filtrate, &c., &c. In deflagrating, the quantity of nitre must be increased to oxidize the sulphur combined with the antimony as well as that with the arsenic :—

1 at. Sb_2S_5, and 7 at. $KO + NO_5$, form
1 at. $KO + Sb_2O_5$, 5 at. $KO + SO_3$, 1 at. $KO + NO_3$, and 6 at. NO_2.

2612 Parts of golden sulphuret require therefore 8855 parts of nitre.

STIBIUM SULPHURATUM RUBRUM.

Antimonii Sulphidum Rubrum.—Red Sulphuret of Antimony.—Kermes Mineral.

FORMULA OF THAT FREE FROM OXIDE:

$$Sb_2S_3 + HO.$$

FORMULA OF THAT CONTAINING OXIDE:

$$(Sb_2S_3 + HO) + x(NaO + Sb_2O_3.)$$

Preparation.—In giving a process, for this preparation, which shall be of general utility, the difficulty arises that almost all of those at present known, yield products of different compositions. The greatest obstacle is the uncertainty whether Kermes Mineral should contain oxide of antimony, and how much? Of course Pharmaceutists are bound to follow such a process as shall yield them, as nearly as possible, a preparation corresponding to that ordered in their own Pharmacopœia. I will now give one good method for preparing the Kermes mineral free from oxide; and one (as far as regards its yield and appearance), to be recommended containing oxide. I have devoted especial attention to the theory of the latter preparation respecting which opinions vary; otherwise this article will be less voluminous than in most text books, for which doubtless my readers are not sorry.

(*a*) *That free from oxide.*—8 Parts of dried and powdered Glauber's salts, 6 parts of powdered sulphuret of antimony, and 3 parts of powdered charcoal are intimately mixed, and fused as under the previous article (*a*), the mass boiled, but without the addition of sulphur, with 30 to 40 parts of water; filtered, and the filtrate diluted with 100 to 150

parts of water, precipitated with dilute sulphuric acid free from arsenic, the precipitate washed and dried at a gentle heat. The product will equal 5—5½ parts.

(*b*) *That containing oxide.*—6 Parts of dried and powdered carbonate of soda, 5 parts of powdered sulphuret of antimony, and 1 part of powdered sulphur are intimately mixed and pressed into a covered earthen crucible, which must be only ¾ filled; then heated in a good wind furnace until its contents quietly fuse, and poured into an iron pot. When cold the mass is powdered, and 100 parts of boiling water, in which the crucible has been previously washed, poured on it and kept boiling with constant stirring for half an hour, that which evaporates replaced with boiling water and filtered into a vessel containing about 2000 parts of lukewarm water. After washing the residue on the filter with hot water, the whole of the liquids are well stirred together in the precipitating vessel, and allowed quietly to deposit for some days; if at the end of this time it has not properly subsided, it is well stirred up, and fresh water added; the precipitate washed by decantation with cold water is collected on a strainer and dried at a gentle heat. It will weigh about 3½ parts. Common water is not admissible for washing this precipitate, and in order to spare the quantity of distilled water, the liquid is sometimes filtered, the precipitate dried with a gentle heat, finely powdered, and treated with fresh quantities of water as long as the latter acquires an alkaline reaction or taste, then dried again.

Recapitulation.—(*a*) The fusion has been explained in the previous article under (*a*). Water dissolves from the mass the hyposulphantimoniuret of sodium formed = $3NaS + Sb_2S_3$, together with any sulphuret of arsenic that may be present, and which at the expense of a portion of the sulphuret of sodium, forms an analogous hyposulpharseniuret of sodium:

the excess of carbon and the sulphurets insoluble in sulphuret of sodium, (iron, copper, lead,) exist in the residue. The filtered solution is (nearly) colourless and does not become turbid in closed vessels. It cannot be freed from sulphuret of arsenic by crystallization, for evaporated in the air it undergoes partial decomposition, one part of the sulphuret of sodium gives up its sulphur to the sulphuret of antimony forming the highest sulphuret $= Sb_2S_5$, which combines with the undecomposed sulphuret of sodium to form sulphantimoniuret of sodium $= 3\ NaS + Sb_2S_5$; (the same salt as that from which the golden sulphuret is precipitated by acids;) as however sufficient sulphuret of sodium is not present for the conversion of all into sulphantimoniuret, a portion of the highest sulphuret just formed is again decomposed, sodium and antimony being set free. This is explained by the following formula:—

4 at. $3NaS + Sb_2S_5$ separate into
8 at. Na, 4 at. NaS, and 4 at. Sb_2S_5;

and these again transpose themselves into

3 at. $3NaS + Sb_2S_5$, 3 at. Na, and 2 at. Sb.

The liberated 3 at. sodium and 2 at. antimony abstract oxygen from the air, forming 3 at. of soda and 1 at. of antimonic acid:—

3 at. Na, 2 at. Sb, and 8 at. O, form
1 at. $3NaO + Sb_2O_5$.

The reaction is more readily explained by supposing that 1 at. of hyposulphantimoniuret of sodium gives up its sulphur to 3 other atoms, which at the same time combine with 8 at. of oxygen:—

4 at. $3NaS + Sb_2S_5$ and 8 at. O, form
3 at. $3NaS + Sb_2S_5$ and 1 at. $3NaO + Sb_2O_5$.

When dilute sulphuric acid comes in contact with the solution of hyposulphantimoniuret of so-

dium, water is decomposed; the oxygen of the water goes to the sodium, forming soda, which combines with the sulphuric acid, the hydrogen with the sulphur of the sulphuret of sodium is given off as sulphuretted hydrogen, and the sulphuret of antimony falls as a red flocculent precipitate :—

1 at. $3NaS + Sb_2S_3$, 3 at. SO_3, and 3 at. HO, form
3 at. $NaO + SO_3$, 3 at. HS, and 1 at. Sb_2S_3.

(*b.*) When carbonate of soda or potash is fused with sulphuret of antimony, the carbonic acid is given off, causing the mass to puff up ; 3 at. of soda deprive 1 at. of sulphuret of antimony of its sulphur, at the same time the antimony and oxygen combine ; the 3 at. of sulphuret of sodium thus formed combine with 1 at. of sulphuret of antimony to hyposulphantimoniuret of sodium, and the 1 at. of oxide of antimony combines with 2 at. sulphuret of antimony to the so-called crocus of antimony (Stibium oxidatum fuscum). The fused mass acquires from its colour the name of liver of antimony, (Hepar antimonii):—

3 at. $NaO + CO_2$ and 4 at. Sb_2S_3, form
1 at. $3NaS + Sb_2S_3$, 1 at. $Sb_2O_3 + 2Sb_2S_3$,
and 3 at. CO_2.

1995 Parts of carbonate of soda should require therefore 8848 parts of sulphuret of antimony. If fused in this proportion, however, only the hyposulphantimoniuret of sodium and any sulphuret of arsenic is dissolved, the crocus of antimony remaining in the precipitate with sulphurets of iron, copper, and lead. In order to obtain a precipitate, simply on cooling, without any addition of acid, the quantity of carbonate of soda must be increased, and, in proportion to this, increases also the quantity of precipitate. The excess of carbonate of soda decomposes the crocus of antimony, (the compound of 1 at. of oxide of antimony and 2 at. sulphuret of anti-

mony,) taking up oxide of antimony, by considerable excess of soda the whole of it, whilst the sulphuret of antimony combines with the hyposulphantimoniuret of soda forming with it an acid salt = $3NaS + 3Sb_2S_3$. We may infer, either that the decomposition of the liver of antimony by excess of soda occurs during the fusion, or only on boiling the mass with water.* One thing is certain, that with a considerable excess of soda, as in the proportions given, the fused mass will be almost entirely dissolved by boiling water, the solution on cooling giving down a dense reddish-brown precipitate. The hot solution, as before stated, contains acid hyposulphantimoniuret of sodium and oxide of antimony dissolved in carbonate of soda. The acid sulphur salt is soluble only in the hot solution, on cooling it separates into the neutral salt, which (together with sulphuret of arsenic) remains dissolved, and free sulphuret of antimony which precipitates as an amorphous hydrate. The oxide of antimony, which also has been dissolved in considerable quantity by the hot solution of carbonate of soda, is at the same time thrown down in a crystalline state chemically combined with soda. The precipitate is consequently a mixture of amorphous hydrated sulphuret of antimony and crystalline oxide of antimony combined with soda. These two constituents appear under the microscope perfectly distinct, the sulphuret of antimony in brown-red globules; the oxide of antimony and soda in white, transparent crystals. In order that the precipitate may be very finely divided, the boiling hot filtrate is at once brought in contact with a large volume of warm water; this causes the precipitate to deposit with difficulty and also require a large volume of water to wash it; by collecting and dry-

* My own experiments lead me to the first supposition; and, (according to Liebig) if 4 parts of sulphuret of antimony and 1 part of soda are fused, and the mass then boiled with solution of soda we obtain, even if the amount of soda exceeded that of the sulphuret of antimony, scarcely 1 part of kermes.

ing the precipitate and then washing, less water is necessary. In washing, cold water must be used, for hot water not only abstracts soda and oxide of antimony, but causes a partial oxidation of sulphuret of antimony. Most of the fused mass dissolving on the first boiling, this process need not be repeated.

The proportions given, viz., 6 parts soda, 5 sulphuret of antimony, and 1 sulphur, equal rather more than 15 at. carbonate of soda to 4 at. of sulphuret of antimony, and in practice we find that the excess of soda (over 12 at.) is sufficient to decompose the crocus of antimony (1 at. oxide of antimony and 2 at. sulphuret of antimony) entirely. The free sulphur (over 8 at.) diminishes the quantity of oxide of antimony, a certain portion of sulphuret of sodium being formed at its expense instead of at the cost of the sulphuret of antimony. Consequently, if the sulphur exceeded a certain proportion no oxide of antimony would be formed; but this cannot happen so long as the soda is in excess. If the proportion of soda much exceeds the prescribed quantity, all the oxide of antimony remains dissolved on cooling, and kermes free from oxide is precipitated.

In the preparation of kermes only 6 parts of carbonate of soda (or a corresponding quantity of potash) and 5 parts of sulphuret of antimony are generally ordered; but the large residue on the filter, (mostly crocus of antimony,) accounts for the small product thus obtained. Having thus explained the formation of the kermes, I will now do so with some secondary products obtained in the process. After boiling the fused mass with water, a residue of glistening metallic particles generally occurs; whilst on the other hand, the liquid from which the kermes has precipitated throws down golden sulphuret of antimony (Sb_2S_5) when treated with acid. These facts are intimately connected; sulphuret of sodium has a great affinity for the highest sulphuret of an-

timony, as however in the present case the quantity of sulphur is insufficient to convert the lowest sulphuret of antimony (Sb_2S_3) into the highest, sulphur is abstracted from a portion of the former, and metallic antimony separates:—

9 at. NaS and 5 at. Sb_2S_3, form
3 at. $3NaS + Sb_2S_5$ and 4 at. Sb.

This compound of sulphuret of sodium with the highest sulphuret of antimony remains dissolved in the supernatant alkaline liquor, and on the addition of dilute sulphuric acid the highest sulphuret of antimony is thrown down, sulphate of soda formed, and sulphuretted hydrogen given off. We must not suppose that the precipitate is simply the highest sulphuret of antimony, as it has already been shown that the alkaline liquor also contains, besides free carbonate of soda, the neutral hyposulphantimoniuret of sodium ($3NaS + Sb_2S_3$) consequently, the lowest sulphuret (Sb_2S_3) is thrown down by the acid, and as the different sulphurets of antimony whilst freshly precipitated and moist have a very similar appearance, an admixture of them is scarcely to be detected by the eye alone.

The so-called wet method of preparing the kermes containing oxide, by simply boiling finely-powdered sulphuret of antimony with carbonate of soda or potash, gives the same product as the dry way, but a far smaller yield of kermes. In this process the sulphuret of antimony is acted on most readily in proportion to the increased concentration of the solution. The mother liquor must be boiled several times on the residue and the precipitates which form each time on cooling, mixed together. This method is in no respects preferable to the dry way.

Properties.—Kermes is a soft, more or less brownish-red odourless and tasteless powder. When free from oxide the colour is darker and if magnified appears as little amorphous globules;

that containing oxide is interspersed with colourless crystals of oxide of antimony and soda. The preparation (*b*) contains nearly $\frac{1}{3}$ of this oxide of antimony and soda. Heated in a test tube kermes mineral loses water, liquifies, and gives off some of its sulphur, which with the water is deposited in the upper part of the tube, leaving a steel-gray mass in appearance like ordinary sulphuret of antimony, yielding, according to the amount of oxide of antimony present, a more or less red powder. The separation of free sulphur on heating is due to the action of the air and water, these at the same time act on a portion of the sulphuret of antimony; oxide of antimony, sulphuretted hydrogen, and sulphurous acid are formed, and, of course, by the mutual action of the two last, sulphur is deposited.

Heated in the open air, most of the sulphur burns to sulphurous acid, leaving a residue of antimonious acid.

Hydrochloric acid readily dissolves Kermes with evolution of sulphuretted hydrogen, the solution is rendered milky by water (*vide* STIBIUM CHLORATUM). A solution of tartaric acid abstracts oxide of antimony, leaving hydrated sulphuret of antimony; the solution thus formed does not become turbid with water. On the other hand, caustic potash dissolves the sulphuret, and leaves the oxide of antimony. In caustic ammonia only $\frac{1}{1120}$ is soluble; cold distilled water agitated with it must not acquire an alkaline reaction, or yield a precipitate with nitrate of baryta, nitrate of silver, oxalate of ammonia, or phosphate of ammonia (*vide* STIB. SULPH. AUR.); in the same article are directions for testing for *sulphuric acid*, *hydrochloric acid*, *lime*, *magnesia*, *carbonic acid*, *silica*, *lead*, *iron*, *copper*, and *arsenic*.

STRYCHNINUM PURUM.

Strychnine.

FORMULA: $C_{44}H_{24}N_2O_4 + 2HO = \overset{+}{Sr} + 2HO$.

Preparation.—From Nux Vomica. Proceed according to the directions under the article BRUCINE. To obtain finer crystals, the strychnine freed from the latter substance is dissolved in 12 parts of hot alcohol of 80 per ct., and the solution placed for 24 hours in the cold. The mother liquor is further evaporated. The yield of pure crystalline strychnine is about 6 drachms from 10 pounds of nux vomica.

Properties.—Strychnine crystallizes in white four-sided pointed prisms, is odourless, and of an insupportably bitter taste. In the air, at the ordinary temperature, or a gentle heat, it undergoes no change, more strongly heated, it fuses to a pale-yellow liquid, gives off white vapours, becomes brown, and burns with a clear flame, leaving a carbonaceous residue, which must be entirely consumed by continued heating. Water dissolves only about $\frac{1}{6666}$ part, but acquires a strong and permanent bitter taste. Alcohol of 80 per ct. dissolves at the ordinary temperature only $\frac{1}{120}$, when boiling $\frac{1}{10}$ of its weight; the solution reacts feebly alkaline. In ether and caustic alkalies it is insoluble. Chlorine water dissolves strychnine, but not completely; ammonia causes in the solution a dense white flocculent precipitate which, on standing, acquires a rose colour. Brucine is best detected by the red colour it imparts to dilute nitric acid, becoming yellow on warming, protochloride of tin then causes a purple-violet colour, and similar precipitate; pure strychnine is unchanged by nitric acid in the cold, and gives on heating a greenish-yellow colour, which

with protochloride of tin yields a white turbidness. *Lime, magnesia*, and other *mineral powders*, are left behind on boiling with spirit of wine, or heating to redness.

STRYCHNINUM NITRICUM.

Nitrate of Strychnine.

\+

FORMULA: $Sr + NO_5 + HO$.

Preparation.—1 Part of pure strychnine is rubbed with 24 parts of lukewarm water, and nitric acid, spec. grav. 1·20, previously diluted with double its weight of water, added by drops; about half the weight of strychnine will be requisite. The salt is very carefully evaporated to crystallization. The product about equals the strychnine employed.

Recapitulation.—Strychnine completely saturates nitric acid, forming a neutral salt:—

1 at. $C_{44}H_{24}N_2O_4 + 2HO$, and 1 at. NO_5, form
1 at. $C_{44}H_{24}N_2O_4 + NO_5 + HO$, and 1 at. HO.

4575 Parts of strychnine require only 2500 parts of nitric acid, spec. grav. 1·20, (=23 per ct. anhydrous). An excess of acid must be avoided, as it exerts a corrosive action on the warm solution.

Properties.—Nitrate of strychnine forms white mother-of-pearl-like needles, permanent in the air, odourless, but excessively bitter. Heated, it puffs up, slightly deflagrates, leaving a carbonaceous mass which must be completely combustible. Water, at the ordinary temperature, dissolves $\frac{1}{50}$, boiling half its weight, alcohol of 80 per ct., $\frac{1}{100}$, boiling half its weight; the solutions have a neutral reaction.

STRYCHNINUM SULPHURICUM.

Sulphate of Strychnine.

+

FORMULA: $Sr + SO_3 + 8HO$.

Is prepared as the preceeding. 4575 Parts of strychnine require 613 parts of hydrated sulphuric acid, which must be diluted. In most respects it agrees with the nitrate, but is soluble in 42 parts cold, its own weight of boiling water; in 82 parts of cold, and its own weight of boiling alcohol 80 per ct.

SULPHUR IODATUM.

Sulphuris Iodidum.—Iodide of Sulphur.

FORMULA: S_2I.

Preparation.—1 Part of washed flowers of sulphur are rubbed with 4 parts of iodine, the mixture warmed in a flask, on a sand bath, until completely liquid. The flask is cooled, broken, and the mass placed in a well-stoppered bottle.

Recapitulation.—Sulphur and iodine combine and liquify on gently warming; 2 at. sulphur and 1 at. iodine correspond to 402 of the first, and 1581 of the latter. The proportion of iodine is slightly increased, as a small quantity is given off in fusing.

Properties.—Iodide of sulphur is a dark-gray radiated metallic-looking mass, the constituents of which are but loosely combined. Gently heated it fuses, evolves violet vapours of iodine, and finally sublimes entirely.

SULPHUR PRECIPITATUM.

Lac Sulphuris.—Milk of Sulphur.

FORMULA: $S + xHS$.

Preparation.—3 Parts of hydrate of lime, 5 parts of powdered sulphur, and 20 parts of water are boiled, with constant stirring, in an iron pot, which must be only $\frac{2}{3}$ full, for one quarter of an hour after the liquid has acquired a dark-yellow colour, then filtered. The residue is boiled, with constant stirring, in 20 parts of water, and filtered to the preceding. When quite cold, the clear solutions are poured into an earthen or wooden vessel, large enough to contain 130—150 parts, diluted with 40—60 parts of water, and hydrochloric acid, free from arsenic, spec. grav. 1·130, mixed with twice its weight of water added until no more effervescence occurs, and a decidedly acid reaction is obtained. 7—8 Parts of acid will be sufficient. From the quantity of sulphuretted hydrogen given off, the operation must be carried on in the open air. When the precipitate has formed, it is washed by decantation with fresh water as long as the latter acquires an acid reaction, and gives a precipitate with oxalate of ammonia. It is then drained, pressed, and dried with a gentle heat. It will weigh $3\frac{1}{2}$ parts.

Recapitulation.—When lime, excess of sulphur, and water, are heated together, the two first combine, forming a readily soluble compound, the highest sulphuret of calcium = CaS_5. The oxygen of 2 at. of calcium combines with 2 at. of sulphur to hyposulphurous acid, which unites with 1 at. of lime, whilst the two at. of calcium take up 10 at. of sulphur:—

3 at. CaO, and 12 at. S., form
2 at. CaS_5, and 1 at. $CaO + S_2O_2$.

1388 Parts of hydrate of lime ($CaO + HO$) require 2400 parts of sulphur, or $2\frac{8}{10}$ of the first to 5 of sulphur. The slight excess of the latter in the proportions 3 and 5 is necessary from the impurities found in lime. The commencement of the boiling is accompanied with an effervescence, consequently the vessel must be large enough, cast-iron will be scarcely acted on. On filtering, a yellowish-white residue occurs, consisting of sulphur, magnesia (from the lime), sulphate of lime (from the oxidation of a portion of the hyposulphite of lime, and sulphuret of calcium), carbonate of lime (from the action of the air on sulphuret of calcium), and iron, together with silica and other impurities of the potash. On adding hydrochloric acid to the filtrate, the following decomposition ensues:—

2 at. CaS_5, and 2 at. HCl, form
2 at. CaCl, 2 at. HS, and 8 at. S.

The highest sulphuret of calcium exchanges its sulphur for chlorine; $\frac{1}{5}$ of the sulphur is given off as sulphuretted hydrogen, in combination with the hydrogen of the hydrochloric acid, whilst the other $\frac{4}{5}$ precipitate in combination with a little sulphuretted hydrogen, forming the so-called milk of sulphur. If the solution is not cooled, the sulphur will precipitate in a compact mass, instead of a light powder. If the hydrochloric acid contain sulphuric acid gypsum will at the same time be precipitated, together with any arsenic it may contain, and thus render the product impure. Soon after the decomposition, the supernatant liquid becomes milky, from the same reason as the solution in the preparation of golden sulphuret of antimony (page 584).

Properties.—Precipitated sulphur is a soft yellowish-white, odourless, and tasteless powder. Exposed to the air it undergoes no change,* at a

* During the drying, from the presence of water it undergoes a slight oxidation, and in consequence acquires an acid reaction.

gentle heat it fuses, evolves a little sulphuretted hydrogen, and now corresponds in every respect to the ordinary sulphur; it is volatile by continued heating. Water and dilute acids are without action on it: fuming nitric acid, as well as aqua regia, converts it into sulphuric acid. Caustic potash, when warm, dissolves it like lime. It dissolves unchanged in sulphuret of carbon, crystallizing from the solution on evaporation. Water should take up nothing from it, any *sulphuric acid* is detected in the solution by nitrate of baryta, *hydrochloric acid* by nitrate of silver, and a *lime salt* by oxalate of ammonia. A residue on heating arises from earthy salts: to determine these it is heated for some time to redness, then treated with hydrochloric acid; if this causes an effervescence, *carbonate of lime* is probably present. A white precipitate caused by liquor ammonia in the hydrochloric solution, and redissolved by solution of potash, indicates *alumina*; a brown precipitate by ammonia, *iron*. The hydrochloric acid solution, supersaturated with ammonia, and filtered if necessary, gives with oxalate of ammonia a precipitate if *lime* is present, and on removing this, one with phosphate of ammonia if *magnesia* occurs. If any of the heated residue is insoluble in hydrochloric acid, but dissolves in a large quantity of water, it is probably *gypsum*; the constituents are determined by the ordinary reagents (oxalate of ammonia and nitrate of baryta). A residue which is taken up only by caustic potash is probably *Silica*. *Arsenic* is best detected by deflagrating the preparation with four times its weight of nitre, by which sulphate and arseniate of potash are formed, supersaturating with sulphuric acid, boiling the solution until all the nitrous acid is evolved, then treating with sulphurous acid to reduce the arsenic acid to arsenious and boiling to drive off the excess of sulphurous acid, when sulphuretted hydrogen

gives a yellow precipitate; (*vide* KALIUM OXID. TART. STIB.) *Organic matter* (meal, &c.) is known by the products of combustion, and carbonaceous residue on heating. *Flour* or *starch* is detected by the blue colour caused with tincture of iodine.

VERATRIUM.

Veratrine.

FORMULA: $C_{34}H_{22}NO_6$.

Preparation.—From Sabadilla seeds. These seeds are freed as much as possible from the hulls, finely powdered, the powder digested in a tin or copper still with three times its weight of alcohol of 70—80 per ct. for one day; strained when cool, the residue pressed and treated twice again with the same quantity of alcohol. The tinctures are allowed to subside, the bottoms filtered, $\frac{1}{6}$ their weight of water added, the alcohol distilled, a considerable quantity of powdered charcoal added to the residue, which is then evaporated with a gentle heat to dryness. The dry mass is finely powdered, treated in a flask with three times its weight of water which contains dilute sulphuric acid, equalling in weight $\frac{1}{100}$ that of the seeds with the hulls, digested for 1 day at a gentle heat, allowed to remain 1 day in the cold, then strained, twice again digested with acidified water, and, after filtering, the acid liquors are precipitated with excess of carbonate of soda. The precipitate is allowed to subside completely, and after decanting, the supernatant liquor thrown on a filter and washed with cold water until this runs off colourless. Whilst still moist it is treated with a large amount of water, dilute sulphuric acid added by drops until entirely dissolved, then digested with purified animal charcoal, filtered, thrown down with ammonia,

the precipitate washed and dried with a very gentle heat. The product from 13 pounds of seeds freed from hulls, will be 5 or 6 drachms.

Recapitulation.—Veratrine exists in the seeds combined with an acid. Alcohol dissolves it together with resin and extractive matter. After separating the alcohol the residue is evaporated to dryness to render the resin perfectly insoluble; the charcoal facilitates the next digestion. Dilute sulphuric acid dissolves the veratrine with some extractive matter and a trace of resin. The alkaloid is thrown down by carbonate of soda, and with it the colouring matter; to remove the latter a second solution in acidified water and digestion with animal charcoal is necessary, and ammonia then precipitates the veratrine entirely pure. It must be dried at a gentle heat, otherwise it agglutinates.

Properties.—Veratrine thus prepared is a tolerably white, light, amorphous powder, of an excessively sharp burning taste, no odour, but its dust causes an intense sneezing and burning sensation in the nose. Warmed, it fuses to a yellow liquid, becoming brown at a higher temperature and giving off white vapours, it then ignites and leaves a coally residue which must be entirely combustible. In water it is insoluble. Alcohol of 80 per ct. at the ordinary temperature dissolves $\frac{1}{3}$, boiling $\frac{1}{2}$ its weight; its solutions react strongly alkaline. Ether dissolves scarcely $\frac{1}{50}$. *Mineral* admixtures are detected by the residue on burning, and *organic* by the large carbonaceous residue.

ZINCUM PURUM.

Pure Zinc.

FORMULA: Zn.

Preparation.—A black lead or earthenware retort is about half filled with commercial zinc. The most

convenient form is that granulated by melting and pouring into cold water which is at the same time well stirred; the zinc must then be well dried. The retort is placed on a brick support in a wind furnace, its neck passed through and luted with clay into a hole in the side of the latter; if the neck of the retort is very short, an iron connector ½ a foot long is attached. An earthen pot filled with water and placed about 6 inches below the beak of the retort serves as a receiver. A small quantity of red-hot coal is placed at the bottom of the furnace, which is then filled with cold coke. As soon as the fuel is of a bright red heat, a stout iron wire is, about every five minutes, thrust up the neck of the retort to loosen any metal that may have distilled and solidified. That which has not solidified in the neck falls in red-hot lumps into the water. The furnace is fed from above. When about one-tenth of the zinc has distilled over the receiver is changed, and the distillation continued until ended. 4 Pounds of zinc, when the fire is not allowed to slacken, will yield, in from 2 to 3 hours, 3½ to 3¾ pounds of pure zinc.

Recapitulation.—The zinc of commerce generally contains some of the following impurities, iron, manganese, cadmium, lead, copper, carbon, sulphur, arsenic, and tin. At the white heat arsenic and cadmium volatilize; the other metals remain behind and together with a little of the zinc oxidize, from the air entering through the pores and neck of the retort. The sulphur and carbon are also given off as sulphurous acid and carbonic oxide. Arsenic distils long before the two other metals, oxidizing at the same time to arsenious acid, then cadmium, and lastly zinc passes over. The first tenth distilled contains all the cadmium with a little zinc, the latter portion is pure zinc. If required simply for Marsh's test and not for making pure oxide of zinc the cadmium is unobjectionable. The zinc as

it distils solidifies in the neck of the retort partly falling in lumps into the receiver and part becoming fixed, which must be constantly raked out, otherwise the neck becomes stopped up, and renders it necessary either to stop the process or break off the end of the retort neck, which is then probably so hot that the vapours of zinc ignite; a small loss from combustion always occurs. The receiver is not placed too close to the beak of the retort, so that the latter may be readily cleared. The distillate is afterwards washed and dried.

The retort will contain as a dirty greenish-yellow powder, the foreign metals more or less oxidized together with a little zinc. I have always found the last portion of distilled zinc free from other metals, the first containing nothing but cadmium.

Properties.—Pure zinc is a lustrous white metal with a bluish-gray tinge, spec. grav. 6·8—7·1. It has a scaly fracture, at the ordinary temperature it is tough although of a slightbrittleness at 250° Fah.; at 300° Fah. it is both malleable and ductile, whilst at 390° Fah. it is so brittle that it may be powdered. At 750° Fah. it fuses, and at a white heat (air being entirely excluded) it volatilizes completely. In the air it gradually loses its lustre, becoming covered with a thin gray coating of oxide, of a similar nature to the scum which forms on fusing; if this last-named scum be removed when the metal is at a bright red heat, the latter ignites and burns with a clear greenish-white flame to oxide. Zinc is readily soluble in dilute sulphuric, hydrochloric, and nitric acids; should the latter leave a white residue which with carbonate of soda before the blowpipe is reduced to a ductile metallic bead *tin* is present; this metal is only oxidized not dissolved by nitric acid. If the same solution acquires a red colour with sulphocyanide of potassium *iron* is present (*vide* BISM. NIT.); a white precipitate with nitrate of baryta is *sulphur* oxidized to sulphuric acid by the nitric

acid. A stinking gas evolved on dissolving in hydrochloric acid is due to *carbon*, if the gas passed into acetate of lead causes a blackening it is due to *sulphur* as sulphuretted hydrogen; whilst a metallic ring, when a pointed tube is fixed to the evolution flask, the gas ignited, and a cold piece of porcelain applied, arises from *arsenic* (*vide* ACID MURIAT.); a garlic odour given off by zinc when heated before the blowpipe on charcoal is caused by this metal. If sulphuretted hydrogen causes in a dilute acid solution of the chloride a yellow precipitate readily dissolved by concentrated hydrochloric acid it is *cadmium* only, a more or less brown one is *lead* or *copper*; to determine which of these it is, the sulphuretted hydrogen precipitate is well washed and dissolved in dilute nitric acid, the sulphur filtered off, water added, and then a solution of sulphate of soda, by which the lead is thrown down as an insoluble sulphate; a trace of sulphate of lead, if this metal is present, is also formed by the action of the nitric acid on the sulphuret of lead, this trace of sulphate remains in solution and only precipitates on the subsequent dilution with water. The liquid filtered from the sulphate of lead is then supersaturated with carbonate of soda, a white precipitate is carbonate of cadmium, which heated on charcoal before the blowpipe is reduced to a metallic state, then volatilizes and forms a brown deposit on the charcoal. A blue tint in the supernatant liquor denotes copper; it is therefore supersaturated with acetic acid, and a few drops of ferrocyanide of potassium added when a chocolate-coloured turbidness confirms it.

Manganese, the best method when this occurs in such traces as not to be detected by ordinary reagents, is to fuse the oxidized metal in a platinum crucible with carbonate of potash, to which it imparts a bluish tinge from the formation of manganate of potash.

ZINCUM CHLORATUM.

Zinci Chloridum.—Chloride of Zinc.

FORMULA: ZnCl.

Preparation.—Hydrochloric acid spec. grav. 1·130 is gradually added to zinc, in small pieces, in a capacious flask until the metal is dissolved. 1 Part of zinc requires about $4\frac{1}{2}$ of acid. The flask must towards the end of the process be warmed in a sand bath. The solution is now digested at a gentle heat for one day, frequently agitating with a few pieces of metallic zinc, then filtered. The sixteenth part of the solution is precipitated with carbonate of soda not in great excess, and after washing, the pasty mass returned to the $\frac{15}{16}$, and chlorine passed into the mixture until the latter smells of it; for 16 parts of zinc 1 part of manganese and 3 parts of hydrochloric acid will be requisite. If, after digesting for 1 day, a filtered portion diluted with water and tested with solution of tannin undergoes no change of colour it is all filtered; on the other hand should the tannin cause it to assume a violet colour, another portion is precipitated with soda, added to the remainder, and the digestion continued for a day. The purified solution is evaporated in a porcelain dish, at first over a naked fire, but when thick, with constant stirring in a sand bath, and the salt whilst still hot transferred to well-closed bottles. The product will weigh nearly twice as much as the zinc employed.

Recapitulation.—Zinc readily and completely dissolves in hydrochloric acid, with formation of chloride of zinc and evolution of hydrogen gas:—

1 at. Zn and 1 at. HCl, form
1 at. Zn Cl and 1 at. H.

407 Parts of zinc require 455 parts of anhydrous or 1750 parts of hydrochloric acid, spec. grav. 1·130. When digested with excess of zinc the lead, copper, cadmium, tin, and arsenic are entirely precipitated, a corresponding quantity of zinc replacing them. Most or all of the arsenic will have volatilized during the solution together with any sulphur or carbon as arseniuretted, sulphuretted, and carburetted hydrogen. The stinking smell of the gas evolved is mainly due to the carburetted hydrogen. A black residue previous to the digestion with excess of zinc is due to carbon. The strange metals are completely thrown down by zinc only on warming; iron and manganese are not precipitated. By carbonate of soda a tribasic salt is thrown down:—

3 at. ZnCl, 3 at. $NaO + CO_2$, and 3 at. HO, form
3 at. NaCl, 1 at. $3ZnO + CO_2 + 3HO$, and 2 at. CO_2.

The carbonate of soda might be added to the whole of the solution, but then the precipitate would not be sufficiently finely divided, and the product would be contaminated with soda. This basic carbonate of zinc precipitates the iron if in its highest state of oxidation or highest chloride, the protochloride or protoxide of iron not being acted on by oxide of zinc. By solution in hydrochloric acid the iron is dissolved as protochloride, which by the after-treatment with chlorine is converted into perchloride; the base of the carbonate of zinc having a greater affinity for this chlorine the iron is thrown down as hydrated peroxide, the carbonic acid evolved and chloride of zinc formed:—

1 at. Fe_2Cl_3 and 1 at. $3ZnO + CO_2 + 3HO$, form
3 at. ZnCl, 1 at. $Fe_2O_3 + 3HO$, and 1 at. CO_2;

the white precipitate (of carbonate of zinc) gradually changing to a brown. A slight loss of zinc always occurs from the necessity of employing an excess to remove all the iron; it is however in-

considerable. By the solution of tannin any iron is detected; sulphocyanide of potassium might be substituted for it. The solution freed from iron yields a white salt. The heat must not be continued after the salt is dry, nor more than a sand heat employed, otherwise a loss from volatilization occurs, and a salt insoluble in water is formed.

Properties.—Pure chloride of zinc is a white crystalline powder, odourless, and of a pungent saline, nauseous metallic taste. It rapidly deliquesces in the air; heated in a platinum spoon it fuses, yielding when cool a grayish-white mass; if the heat is continued, thick white vapours are given off, leaving finally a white mass, which whilst hot appears yellow, but on cooling quite white, or with only a slightly yellow tinge. This residue is oxide of zinc with a trace of chloride of zinc which cannot be removed by heat. The neutral chloride of zinc does not volatilize as such, but separates into a volatile acid and a fixed basic salt; whilst a part becomes decomposed, chlorine is given off and the metal acquires oxygen. The salt is readily soluble in water, alcohol, and ether; the solutions have an acid reaction; if they contain white flocculent matter this is *oxide* of *zinc*, with a trace of chloride, from heating too strongly. The aqueous solution with a little acetic acid should give no violet colour (*iron*) with tannin. Tannin gives a dirty-white precipitate of tannate of zinc in the pure solution which is dissolved by acetic acid. A precipitate by chloride of barium as due to *sulphuric acid*. If sulphuretted hydrogen is passed into the solution acidified with hydrochloric acid, and causes a yellow precipitate soluble in concentrated hydrochloric acid *cadmium* is present; if it appears more or less brown it is washed, digested with hydrosulphuret of ammonia and filtered, the filtrate evaporated to dryness in a platinum spoon and heated to drive off all the sulphur; a yellowish-white powder remaining is *tin*.

This metal is thrown down as a sulphuret which is soluble in hydrosulphuret of ammonia; the ammoniacal salts and sulphur are driven off by heating, the tin being converted into oxide remains. If the hydrosulphuret of ammonia leaves a residue, test for *copper*, *lead*, and *cadmium*, as in the preceding article, by dissolving in nitric acid, &c. *Arsenic* will have entirely volatilized, and for *Manganese* refer to preceding article.

ZINCUM OXIDATUM.

Zinci Oxidum.—Oxide of Zinc.—Flowers of Zinc.

FORMULA: ZnO.

Preparation.—(*a*) *By the dry method.*—A hessian crucible is ⅓ filled with pure distilled zinc and placed obliquely in a wind furnace, in such a manner that the lower part rests on its edge on a piece of tile at the bottom of the furnace, whilst the upper part is supported on the edge of the furnace; then apply the fire. As soon as the zinc is fused and at a red heat, the scum is continually removed with an iron spatula, the zinc now becomes inflamed and continues so, with the above precaution, as long as any metal remains. The oxide is removed to an iron plate to cool, and more zinc added. The oxide of zinc is rubbed to a thin pasty mass with water in a porcelain dish, this is added to a large quantity of water which after subsiding a minute or two is decanted, more water poured on the grayish-white residue, and this repeated as long as the water becomes milky; care must be taken that none of the metallic particles are poured off with the liquid; the latter is allowed thoroughly to subside and decanted, the residue collected on a linen strainer, pressed and dried at a gentle heat. The yield is about equal to the weight of zinc employed.

(*b*) *By the moist way.*—A quantity of pure sulphate of zinc is dissolved in 30 times its weight of hot distilled water, in a vessel only half filled, and a hot concentrated solution of carbonate of soda added so long as a precipitate is formed; equal parts of both salts crystallized will be sufficient. The precipitate is washed by decantation with warm water, as long as the latter yields a precipitate with chloride of barium, then collected on a linen strainer, pressed, and dried; it is now powdered, and heated to redness in a Hessian crucible, until a cooled portion no longer effervesces with dilute sulphuric acid. 16 Parts of sulphate of zinc will yield about 5 parts of oxide.

Recapitulation.—(*a*) Zinc fuses far below a red heat, but instantly becomes covered with a gray pellicle, which may be considered as a sort of suboxide. At a red heat, when this pellicle is removed, the metal breaks out into a bluish-white luminous flame, from the energetic combination with the oxygen of the air; the luminosity arises from the presence of the glowing, hot, solid particles of oxide of zinc. If, by the constant removal of the oxide formed, free access of air is allowed to the fused metal, it gradually becomes entirely oxidized. If commercial zinc is used, the product will be impure, from the foreign metals also oxidized. To remove the oxide with readiness, the crucible is placed obliquely in the furnace. A part of the oxide formed is so light that it floats away in the air and is lost; this was formerly called Lana philosophica. With the oxide, as removed from the crucible, is mixed a portion of metal, or suboxide, from imperfect oxidation; these particles, from their density, subside more readily than the lighter oxide, and are thus got rid of; by treating it in this way several times the whole of the oxide is removed. On account of this loss, and that by volatilization, the weight of product does not exceed that of metal employed.

(*b*) Carbonate of soda precipitates from sulphate of zinc a snow-white basic carbonate of zinc, a large portion of carbonic acid being given off, and sulphate of soda remaining in solution:

3 at. $ZnO + SO_3 + 7HO$, and 3 at. $NaO + CO_2 + 10HO$, form
1 at. $3ZnO + CO_2 + 3HO$, 3 at. $NaO + SO_3$, 2 at. CO_2, and 48 at. HO.

5385 Parts of crystallized sulphate of zinc require 5370 parts of crystallized carbonate of soda. On account of the carbonic acid which is given off, the precipitating vessel must be only half filled, and the soda added by degrees. If precipitated hot, the carbonic acid is more readily evolved, and the precipitate, being less voluminous, is more easily washed. After well washing and drying, the precipitate is heated to redness, to drive off the carbonic acid and water of hydration; by first rubbing to powder, this process is shortened. On testing for carbonic acid, the (cold) oxide must be added to the acid, and not *vice versâ*; in the first case, from coming in contact at once with an excess of acid, the whole of the carbonic acid is given off. If added to the acid when red-hot, a hissing, readily mistaken for effervescence, will occur.

The mother liquor will contain a small portion of oxide of zinc, dissolved; it is removed by evaporation and crystallization; the sulphate of soda should however be tested with hydrosulphate of ammonia before using.

The common sulphate of zinc from smelting works is unfit for making pure oxide, as it contains magnesia; the latter may be separated but the process would be too expensive.

Properties.—Pure oxide of zinc is a milk-white, tolerably light, odourless, and tasteless powder. Exposed for some time to the air, it attracts carbonic acid and should therefore be kept in closed bottles.

At a red-heat it acquires, without further change, a yellow colour which on cooling again disappears; at a stronger heat it fuses to a yellow glass. Heated on charcoal before the blowpipe, it is reduced and volatilizes completely; a small portion condensing forms a yellow ring on the cold charcoal, becoming white on cooling.

In dilute sulphuric, nitric, and hydrochloric acids it is readily soluble, if with effervescence carbonic acid is present. A gray colour indicates metallic particles (from its being prepared by the dry way and not thoroughly washed). Water digested with it should yield, when filtered and evaporated, no residue; should any occur and effervesce with dilute acids, it is *carbonate of soda* from imperfect washing. If the oxide, exhausted with water, effervesces with dilute acids, it contains *carbonate of zinc*, from insufficient heating or afterwards exposing to the air, or else *carbonate of lime* or *magnesia;* to determine if it is either of the latter, the nitric acid solution of the oxide is supersaturated with ammonia, precipitated with hydrosulphuret of ammonia, filtered, the excess of hydrosulphuret of ammonia driven off by boiling, and oxalate of ammonia added, a precipitate is *lime;* after filtering this, any precipitate caused by phosphate of ammonia will be *magnesia*. If the residue, left by evaporating the water boiled on the oxide of zinc, gives when supersaturated with nitric acid a white precipitate with nitrate of baryta, *sulphate of soda* is present; if the portion insoluble in water when dissolved in nitric acid gives a white precipitate with nitrate of baryta it contains *basic sulphate* of *zinc*, from incomplete precipitation with carbonate of soda. If the nitric acid leaves a white residue, soluble in caustic potash, it is *silica*. *Tin*, *iron*, *lead*, *copper*, and *cadmium* are detected as under the article ZINCUM PURUM. Arsenic cannot be present.

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ZINCUM OXIDATUM ACETICUM.

Zinci Acetas.—Acetate of Zinc.

FORMULA: $ZnO + \bar{A} + 3HO$.

Preparation.—2 Parts of dry carbonate of zinc are warmed in a flask, and concentrated acetic acid, spec. grav. 1·045, added gradually, until it is entirely dissolved. 5 Parts of acid will be requisite. The solution is filtered warm, and set in a cool place. After a day or two, the liquor is poured off and evaporated to further crystallization. The crystallized salt is spread on filtering paper, and dried at the ordinary temperature. The weight will be nearly double that of the carbonate of zinc employed.

Recapitulation.—Under the article ZINC. OXID. we have considered carbonate of zinc as a compound of 3 at. of oxide of zinc, 1 at. of carbonic acid, and 3 at. of water. Acetic acid dissolves the oxide, and drives off the carbonic acid:—

1 at. $3\,ZnO + CO_2 + 3HO$, 3 at. $\bar{A}$, and 6 at. HO, form

3 at. $ZnO + \bar{A} + 3HO$, and 1 at. CO_2.

2134 Parts of carbonate of zinc require 1914 of anhydrous, or 5316 parts of acetic acid, spec. grav. 1·045 (containing 64 per ct. of water.) The action of the acid is promoted by gently warming.

Properties.—Acetate of zinc crystallizes in white, oblique, rhombic tables, of a considerable size, and silky lustre, smelling feebly of acetic acid, and possessing a bitter, saline, nauseous taste. It remains unaltered in the air, or only slightly effloresces; heated it fuses, loses water, then blackens, giving off empyreumatic products; the zinc becomes reduced, but from access of the air bursts into a bluish-white flame, and burns to oxide. It is

soluble in 3 parts of water, at the ordinary temperature, and in ½ a part of boiling water; in 30 parts of alcohol of 80 per ct. at the ordinary temperature, and 1 part when boiling; the solutions have an acid reaction. For impurities refer to ZINC. CHLOR.; chlorine is detected by nitrate of silver.

ZINCUM OXIDATUM SULPHURICUM.

Zinci Sulphas.—Vitriolum Album.—Sulphate of Zinc. —Zinc Vitriol.—White Vitriol.

FORMULA: $ZnO + SO_3 + 7HO$.

Preparation.—3 Parts of concentrated sulphuric acid are mixed with 15 parts of water in a leaden vessel, and whilst still warm 2 parts of commercial zinc, in small pieces, are added, and allowed to stand, with frequent agitation, for a few days; the vessel is then gently warmed until no further action is perceptible, then ⅛ the weight of zinc already employed added, digested for a day or two, and filtered whilst hot. The solution is diluted to 32 parts with water, and 2 parts removed; these are precipitated with carbonate of soda, and the process given under ZINC. CHLOR., to remove any iron, exactly followed. The chlorine from ⅔ part of hydrochloric acid and ⅛ part of manganese, will be sufficient for 2 parts of zinc. The solution of sulphate of zinc thus obtained is evaporated in a porcelain dish, the crystals dried on filtering paper, at the ordinary temperature, and kept in a cool place. The mother liquor is thrown away. From 2 parts of zinc, 8 parts of crystallized sulphate are obtained.

Instead of pure sulphuric acid, the residue from the distillation of ether previously diluted to spec. grav. 1·125 may, in this case, be employed;

care must, however, be taken that excess of metallic zinc remains behind.

The direct formation from the metal is less expensive than purifying the common white vitriol of commerce.

Recapitulation.—Dilute sulphuric acid dissolves metallic zinc readily, with evolution of hydrogen from the decomposition of water, the oxygen of which combines with the metal, and the oxide thus formed unites with the sulphuric acid, and a certain portion of water:—

1 at. Zn 1 at. $SO_3 + HO$, and 7 at. HO, form
1 at. $ZnO + SO_3 + 7HO$, and 1 at. H.

407 Parts of zinc require, independently of the water necessary for dilution, 613 parts of hydrated sulphuric acid. Most of the zinc dissolves in the cold, the remainder on warming. The disagreeable odour of the gas evolved is principally due to carburetted hydrogen (CH_2) from carbon chemically combined with the zinc. Sulphur or arsenic, if present, is given off at the same time. Carbon, existing only mechanically mixed with the zinc, is thrown down as a black powder. When the ether residue is employed, a considerable quantity of carburetted hydrogen is formed, from a carbonaceous matter it contains in solution (and to which its colour is due), this gives up its carbon to the hydrogen, and the liquid becomes decolourized. Other metals present dissolve with the zinc, but on the addition of an excess of the latter metal, they are again precipitated in the metallic state, excepting iron and manganese, an equivalent portion of zinc replacing them. The precipitate may contain, besides excess of zinc, carbon, lead, copper, cadmium, tin, and perhaps arsenic. This precipitation must be promoted by continuous stirring, and a gentle heat. The precipitation with soda, and removal of the iron, has already been thoroughly

explained under Zinc. Chlor. A slight difference in this case occurs on treating with chlorine, viz., that part of the iron, instead of being simply converted into a higher chloride, acquires a higher degree of oxidation, a portion of perchloride is formed at the same time, thus :—

6 at. $FeO + SO_3$, and 3 at. Cl, form
2 at. $Fe_2O_3 + 3SO_3$, and 1 at. Fe_2Cl_3;

and the oxide of zinc, being the stronger base, combines with the sulphuric acid and chlorine, the persalt and perchloride of iron precipitating as a hydrated peroxide, whilst carbonic acid is evolved :

2 at. $Fe_2O_3 + 3SO_3$, 1 at. Fe_2Cl_3, and 3 at. $3ZnO + CO_2 + 3HO$, form
6 at. $ZnO + SO_3$, 3 at. ZnCl, 3 at. $Fe_2O_3 + 3HO$, and 3 at. CO_2.

On crystallizing, the chloride of zinc and any manganese present, remain in the mother liquor, and are thrown away.

Properties.—Pure sulphate of zinc forms colourless, right-rhombic prisms; it is odourless, and of a sharp, saline, bitter, nauseous taste. It slightly effloresces in the air. Heated it fuses, loses water, again becomes dry, and at a red heat gradually loses all its acid, leaving pure oxide of zinc as a residue; to remove the last portions of acid, a powerful and continued heat is however necessary. It dissolves in 2½ parts of cold, and in less than equal parts of boiling water; its solution reacts acid; alcohol does not dissolve it. *Iron*, *cadmium*, *copper*, *tin*, and *manganese* are detected by the methods under the article Zincum Chlor.: *lime*, and *magnesia* (from the latter, common white vitriol is never free), as under Zinc. Oxid.; *chlorides* by sulphate of silver. *Arsenic* and *lead*, the latter from the sulphuric acid, cannot be present in the crystallized salt. In testing for iron, it is not necessary, as with chloride

and acetate of zinc, to add acetic acid, tannin solutions causing no precipitate in solution of pure sulphate of zinc.

ZINCUM OXIDATUM VALERIANICUM.

Zinci Valerianas.— Valerianate of Zinc.

FORMULA OF THE ANHYDROUS:

$$ZnO + C_{10}H_9O_3 = ZnO + \bar{V}a.$$

FORMULA OF THE HYDRATED:

$$ZnO + C_{10}H_9O_3 + 12HO = ZnO + \bar{V}a + 12HO.$$

Preparation.—1 Part of pure valerianic acid (the terhydrate) is dissolved in a flask with 90 parts of water, ½ a part of carbonate of zinc, freshly precipitated and in a moist state (6 parts of basic carbonate equal 15 of sulphate of zinc, *vide* ZINC. OXID. ALB.) added, digested at a moderate temperature for some hours in a sand bath, then allowed to cool, filtered, and evaporated to half. The salt which separates is strained from the liquor whilst still warm, and the latter evaporated lower. The salt is dried at a gentle heat; it will weigh about 1 part.

The hydrated salt is obtained when freshly-precipitated and well-washed carbonate of zinc is made into a thin paste with water, the pure valerianic acid added, without more water, in the same proportion as before, and the mass dried at a gentle heat.

Recapitulation. — Carbonate of zinc, especially when freshly precipitated, is readily dissolved by an aqueous solution of valerianic acid, valerianate of zinc being formed, and carbonic acid evolved:—

1 at. $3ZnO + CO_2 + 3HO$, and 3 at. $\bar{V}a + 3HO$, form

3 at. $ZnO + \bar{V}a$, 12 at. HO, and 1 at. CO_2.

2134 Parts of basic carbonate of zinc, require 4500 parts of the terhydrated acid, the action is promoted by a gentle heat, a strong heat is disadvantageous, as the salt dissolves more readily in cold than hot water; for this reason sufficient water for its solution in the cold is employed; it can be obtained in the dry state only by evaporation, and of course is not thrown down from a hot solution on cooling; for the same reason, it is better to separate the crystals from the solution whilst warm. If, during evaporation, the solution is allowed to boil, the salt adheres to the bottom of the dish, instead of being obtained in a loose finely-divided state.

Properties.—Anhydrous valerianate of zinc crystallized in snow-white, exceedingly light, plates of a mother-of-pearl lustre, and resembling boracic acid; it smells faintly of the acid, and possesses a bitter metallic taste, combined with that of valerian. Heated it fuses, gives off thick white vapours, ignites, burns with a bluish-white flame, leaving pure oxide of zinc, mixed with a little metallic zinc, which burns, and the heated particles of oxide impart the luminosity to the flame. It dissolves in 90 parts of water, at the ordinary temperature, and in 60 parts of alcohol of 80 per ct.; the solutions have an acid reaction, become turbid when warmed, and clear again on cooling. Cold ether dissolves $\frac{1}{300}$, boiling ether $\frac{1}{20}$ its weight.

The hydrated salt is not different in appearance from the anhydrous; at 212° Fah. it loses its water, or 44 per ct. in weight; it dissolves in 44 parts of cold water; if this solution is evaporated at a boiling temperature, the anhydrous salt crystallizes out.

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